

# **CHEMISTRY**

## **IN HEALTH**

**SIXTH EDITION**

# AND DISEASE

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## PREFACE TO THE SIXTH EDITION

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THE Sixth Edition of *Chemistry in Health and Disease* represents no change in the size of the book. This was accomplished by carefully evaluating the Fifth Edition, and then deleting and condensing some of the subject matter to provide space for new material and for added emphasis on several topics. The first two chapters in Part II, *Organic Chemistry*, have been expanded to three chapters, and the material has been largely rewritten and reorganized. This has been done because the fundamentals of *Organic Chemistry* are becoming increasingly important for an understanding and interpretation of the chemistry of body processes, both in health and disease. The topic of colloids, in the chapter on *Solutions*, has been extensively revised for this new edition.

The features that contributed to the wide acceptance of the previous editions by both students and instructors have been retained for the most part in the present revision. A chapter outline, useful to both the student and his instructor, is placed at the beginning of each chapter. The self-testing questions interspersed throughout the text provide the student with a means of determining his or her understanding and retention of the subject matter. Included in the "Suggested Activities" at the end of each chapter are: "Thought-Provoking Questions," "Vocabulary of New Terms," and "Topics for Oral or Written Reports." Following Parts I, II, and III are reviews of definitions and meanings of significant terms. The laboratory exercises constitute Part V of the book, and they are correlated with the chapters. Part IV consists of an appendix containing charts, tables, and other organized data useful to the chemistry student.

The objective of the Sixth Edition, as of prior ones, is to give the student a foundation in chemistry which will include the necessary chemical facts and theories important in an intelligent approach to the study of health and disease.

Suggestions and criticisms from instructors who have examined this book have always been welcomed, these are valuable guides for revisions. Grateful acknowledgment is given to Dr Alfred H Free, chief chemist and head of the Biological Department of the Miles Laboratories, for the chapter on hormones. Suggestions from numerous correspondents, especially Sister Veronica, of Good Samaritan Hospital, Dayton Ohio, have helped greatly in making the text what it is. The authors also wish to express appreciation to the staff of the F A Davis Company for continued cooperation, and to numerous individuals and organizations to whom they are indebted for permission for use of certain illustrations, as acknowledged throughout the book.

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## PREFACE TO THE FIRST EDITION

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THERE are many life situations in which an applied course in Chemistry is needed. In such instances, all of the ramifications of the science, such as its applications to the industries, are not needed. The medical student, for instance, is very much concerned with biological chemistry, as is the dietitian and student of nutrition, as well as the nurse. Again, there are many public health workers, and numerous technicians of various kinds who are not nurses, and yet are concerned with the application of chemistry in Health and Disease. It is true, that of all such groups, the nurse is the most vitally interested in such an application of Chemistry as that presented in this text.

The author feels that students taking an applied course in Chemistry need only a minimum of inorganic chemistry, especially as the importance of physiological chemistry is being more and more emphasized. At first glance, an instructor may feel that some topics in inorganic chemistry have been entirely eliminated from the text, whereas they are sufficiently covered in the Laboratory Work provided for each chapter.

*Chemistry in Health and Disease* has been divided into three major sections: inorganic, organic, and biochemical. The inorganic section is, of course, a necessary review for the entering student, however, it has been made into a functional discussion, as a consequence this section contains much useful information not ordinarily contained in many texts dealing with elementary inorganic chemistry. Moreover, since practically all of the principles of chemistry are considered in inorganic chemistry, this branch of chemistry must assume a prominent place in any text of this kind.

This text provides sufficient material for a sixty to a ninety hour course and it presents a more extended development of organic chemistry than is given in any other similar text. That the student who has not had much of a background in organic chemistry might

better understand the principles of biochemistry, more than the usual discussion has been allotted to the development of organic principles, and in particular the chemistry of the carbohydrates, fats, and proteins. Much stress is laid upon biochemistry, which of course includes the chemistry of the blood and of the excretory products of the body, as well as chemical changes involved in metabolism, the role of vitamins in nutrition, and the chemistry of milk and other food products. More attention has been given to the chemical changes taking place in the body than has hitherto been presented in a text of this character.

It is a pleasure to acknowledge the author's indebtedness to Dr Cecil E. Boord, Professor of Organic Chemistry, Ohio State University, for his constructive criticism of the chapters included in the organic section of this text, and to Frederic T. Jung, Ph.D., M.D., Associate Professor of Physiology, Northwestern University, for the improvement resulting from his criticisms of the chapter on Metabolism.

My sincere thanks and appreciation for the improvement of this text are due Dr. Anthony Sindoni, Jr., of Philadelphia, Pa., for his excellent fund of information and his personal contribution in writing the chapter on Vitamins.

Especial appreciation should be expressed to Miss Marion G. Howell, Dean of the Frances Payne Bolton School of Nursing, Western Reserve University, who made possible the opportunity to present this material in manuscript form to the author's classes.

# **AN EFFECTIVE METHOD OF STUDYING CHEMISTRY**

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SINCE the greater part of the time devoted to any course is spent in preparation, it is necessary that the student form correct study habits for the assimilation of textbook material. In undertaking a study of any subject one certainly must have a knowledge of the objectives involved. These include the nature of the subject matter to be mastered, and a clear understanding of the facts and principles needed for dealing with the problems embraced in the subject.

Some of the factors in an effective method of studying chemistry have been established by an investigation of the study habits of numerous students who were successful in mastering this science. The following outline of the objectives in this course, together with suggestions for more effective study, should prove helpful

## **I. FACTS AND PRINCIPLES**

- (a) To know that many of the happenings in everyday life as well as hospital procedures are the result of chemical changes, and that our very existence depends upon them.
- (b) To understand the electrical nature of the atom and the principles involved in chemical changes
- (c) To know the properties, uses, and behavior of certain elements, compounds, and classes of compounds
- (d) To have a better understanding of the place and possibilities of chemistry in health and disease

## **II. ATTITUDES**

- (a) To develop a growing understanding of the practical applications of chemistry which furnish so many modern comforts
- (b) To have a desire to select and learn the facts and principles which are necessary for the understanding of chemistry in the field of nursing
- (c) To appreciate the value of health and to demand pure foods, drugs, and other substances necessary to health and social well being
- (d) To appreciate the numerous applications of chemical changes

- (e) To develop a desire to learn the fundamentals of chemistry to the end that the current literature relating to the nursing profession may be read intelligently
- (f) To develop an appreciation of the contributions that chemistry makes for the student's full development

### III HOW TO STUDY

#### **Study Where There Are No Interruptions**

It is much easier to concentrate where it is quiet and where there are likely to be no interruptions. In other words the right environment not only assists you in developing good study habits but aids in conserving time and time is one of the most valuable things in life. Each individual has 24 hours per day, no one has more. Time must be used where it is found. You cannot borrow two hours from today and use it tomorrow. Also time lost can never be regained. For these reasons plan to use your time wisely. Plan your work and then work your plan. Make a class and study schedule, and adhere to it. Experiences of student nurses indicate that finding sufficient time is a most important problem.

#### **Consider the Value of the Subject**

Before beginning to study ask yourself whether the subject matter will be useful to you not only in succeeding courses but also in the future practice of your profession. Only in this way can you stimulate and arouse sufficient interest to have a desire to master your assignments. If at any time interest lags and day dreaming begins think again of the handicaps that must be overcome by a nurse who is lacking in the fundamental principles of chemistry.

#### **Acquire a Bird's eye View of Each Assignment**

For those students who have had some previous training in chemistry it will be sufficient to read the *Chapter Outline* at the beginning of each chapter in order to gain a survey of its subject matter but for those who have had no previous chemistry it will be necessary to read not only the paragraph headings but perhaps the entire chapter. This should be done rapidly. The object is to gain a general idea of the main points of this chapter before beginning to study its details.

#### **Make an Analytical Reading of Each Paragraph**

(a) Underscore the main points or make a marginal note of them. (b) Give special attention to italicized words. (c) Learn the meaning of technical words such as atom and electron. (d) Build a vocabulary of chemical words for quizzing purposes. (e) Master a paragraph before proceeding to the next one.

#### **Question Yourself on the Contents**

Go back, and after looking at the paragraph heading try to recite its essential facts or check your accomplishment by the *Self Testing Questions*. Repeated

recitation is a more effective method of remembering than merely reading the assignment over and over again

### Prepare for Tests

Make up questions (preferably completion type) covering the main points and those other points which you would bring up if you were the instructor. Sometimes it is an advantage to be quizzed by another student. The next best practice is to answer the author's questions

### Study Plans:

(a) Go over your assignment or lecture notes the day they are given. This enables one to remember and plan for study time. (b) Study the assignment the day before going to class. (c) Review underscored lines, italicized words, and your notes the next morning, or just before going to class

## IV. IMPROVING YOUR MEMORY

Everyone spends hours trying to remember things. Maybe it's a name, some statement you read, or something you were supposed to do. You try to concentrate, to pull the thought out of the recesses of your mind. But there are no real muscles that you can use to draw a memory from the past. The harder you try to remember in that manner, the more likely you are to forget. To illustrate, suppose that when being introduced to someone, you are aware of the blue color of his suit, his red necktie, and his mustache. Later, in trying to remember his name, you think of these details and what happens? You cannot recall it. Why? Because your mind is crowded with these details that only serve to detract from the name you want to remember. There has been no association between the man and the name.

### Association Aids Remembering

Instead of this haphazard method, make these details help you. Immediately following the introduction, begin to tie them all together by associating them with something definite about the person. They will have a tendency to stay together. Then, when one fact comes into your mind, they are automatically all brought to the surface. If the man's name in the above incident was Skye, for example, it would be a simple matter to associate the name Skye with the blue color of his suit by merely associating blue and Skye. BlueSkye. It sounds silly, but it does aid remembering. In this simple plan for remembering, you have pictured a detail you wish to recall. Mind pictures are more easily remembered than anything else. To recall anything, you must first give sufficient attention to the facts you wish to remember, and second, learn as many related facts and ideas as you can, so that any one will recall all the others.

### How to Retain What You Read and Study

Sometimes you find after reading a page, your text for example, the inability to recall a single line. The usual reason is that you have read too rapidly, skipped words here and there, let your mind wander occasionally about some



thing else or maybe were not in the right frame of mind, worried for instance. To overcome one or more of these bad reading habits especially lack of concentration and be able to retain textbook material for example you must

**First** Learn to read *slowly*, only one thing at a time (no skipping), and keep your mind on the understanding of each sentence before passing onto the next sentence. By reading slowly your mind's eye can coordinate with your visual eye and then you will have a mental moving picture of what ideas the author is presenting, a principle long ago presented when the Chinese stated that "One picture is worth a thousand words." To retain what you wish to remember you must use a mental moving picture of what you want to remember and associate it with something that is already present in your mind.

**Second** *Underscore the main points or make a marginal note of them.*

**Third** Check your retention by raising your eyes at intervals from your reading and find out how much you can recall. If unable to make a rapid mental moving picture, a glance back at the reading will let you know how well you are concentrating and retaining the subject matter. And for emphasis again you must understand and master a paragraph before proceeding to the next one for if you cannot remember at this point in your reading, what chance do you think you will have of remembering in a coming recitation or written test?

**Fourth** Frequently glance back over the main points and at future times acquire the habit of reviewing. Interval reviewing to memorize requires about one half the time as does one reading.

### **Sometimes You Forget in Order to Remember**

However, it is after really learning something, you still cannot recall it. Try hard to forget it, the secret of accomplishment being to expel it by substituting a more powerful thought. Clear your mind of what is blocking it, and keep it cleared.

Sometimes you will make an intense effort to quickly recall something, and succeed in doing it. But the next time you will find it harder to recall. You may even be unable to recall it at all. This is due to overloading your mind with unrelated details.

When the trick of forgetting unrelated details becomes part of your memory method, you will amaze yourself with the variety of things you can recall. Your very efforts thus far have hidden them from view. If you can't recall something at once, leave it alone, do something else so you will forget it. Later, try a second time. If that doesn't work start forgetting again. Once this becomes a habit, you will have no difficulty in recalling instantly almost anything you once learned.

### **There Are Three Laws of Memory**

**INTEREST** is the first of three great laws of memory. You can learn any thing that you are sufficiently interested in. Since learning is necessary for remembering, the deeper the interest, the more readily you can remember.

The student who can't learn chemistry or any other subject is not very much interested in it. Chances are very little will be remembered unless interest is aroused.

**SELECTION** is the second great law of memory. If you did not forget almost everything, you could not remember anything. Of the countless impressions received by your mind every hour, it is necessary to retain only a select few. Otherwise your mind would constantly be in a state of chaos. Building up a strong memory does not mean remembering everything.

**ORGANIZATION** is the third and most important law of memory. You must center your knowledge around one definite goal, nursing, for example, and keep it in mind always.

From this we can see how all three laws—interest, selection, and organization—depend upon each other, and must work together to give you knowledge and a strong memory.

### **Immediate Reviewing Saves Hours of Study**

Acquiring the habit of review is of major importance in improving your memory. When reviewing anything you want to remember, do it at once, the same day. Otherwise, you will spend two or three times as long the next day. Re-read it a day later, and, after a week, a quick glance at it will suffice to refresh your memory.

As a matter of future consolation, your memory does not become dim with age. It takes you longer to organize your thoughts but your mental power is the same.

## INTRODUCTORY NOTES

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### TO THE INSTRUCTOR

IT MAY be helpful to offer, briefly, what has been found to be a very satisfactory method of presenting the subject of Chemistry to student nurses. The nature of the work expected, and some of the things required of the student, may be presented to the students as a preliminary to beginning the study of chemistry. It is *not* advisable, however, to reveal all that will be expected of the chemistry student, any more than it would be to try to tell a child all that life expects of him. Many things should be presented gradually, and as the work progresses, otherwise the student may become confused and discouraged.

### CLASS WORK

(1) **THE TEXTBOOK:** A textbook is an educational tool. No attempt should be made to use such a tool until the student becomes familiar with it. Explain the organization of the book, beginning with the table of contents. Show the principal divisions of the text and their nature. Now examine one of the chapters showing its organization, its preliminary material, its lesson plan, and its study aids at the end of the chapter.

The first division of this text, *Inorganic Chemistry*, takes up some of the accomplishments of chemistry in providing for greater health, comfort, and leisure. It gives (1) a somewhat elementary conception of the meaning of chemistry, (2) some idea of the accomplishments of the chemist in a changing civilization, (3) an understanding of the chemist's working terms, (4) a mental conception of the electrical nature of the atom and its behavior in chemical changes, (5) a knowledge of the properties and uses of oxygen, water, acids, bases, salts, and certain nonmetallic elements, and (6) the behavior of these elements or compounds under varying conditions.

The second division of this text, *Organic Chemistry*, stresses concentration on certain type reactions applicable to each of the homologous series mentioned. The type equations, together with the examples which accompany them, illustrate the chemistry of other members of the series. In this way students become familiar with the characteristic properties of each series, and do not have to learn too many equations other than the type equations.

The third division of this text, *Biochemistry*, aims only to give students the essential background and facts necessary to understand and evaluate any future accomplishments in this field of work.

This text is designed to enable students to study without any interpretation on the part of the instructor, thereby stimulating the student's interest. Human interest is one of the major principles of education, and without it one remains a poor student.

Interest is the essence of scientific thinking. Teaching difficulties, as usually met, are made somewhat easier by introducing practical helps for both student and instructor.

The outline at the beginning of each chapter simplifies and classifies the subject matter.

The "self testing" questions at the end of the natural breaks in each chapter are such that when properly answered they will assure the student that the minimum essentials have been mastered. The "thought provoking" questions in the Suggested Activities are primarily for those students who can think in the realm of chemistry. These questions are mostly of a practical nature, and have been asked with a view not only of fixing the basic facts developed in the text, but also to enable the student to solve future problems based upon these principles. Since the answers are not directly stated, these thought provoking questions should develop individual thought and research on the part of the student. To provide further for individual differences and to facilitate individual work there are special topics and suggestions.

The important technical words or terms as they first appear in the discussion are listed at the end of each chapter under the title, "vocabulary testing of new terms." This list will be helpful to students who have formed the habit of looking up words that are not familiar to them.

The "topics for oral or written reports" are primarily for students who are capable of doing additional work, especially for those who have had a year's work in elementary chemistry. The reference books and periodicals listed on page 633 should prove helpful as sources of material for such reports. These references, and others, are to be found in most science libraries.

Interest in the course will be aroused by asking the pupils to present any clippings from current periodicals of a chemical nature. These should be signed by the donor and attached to the Chemistry Bulletin Board.

The illustrations, far in excess of those in other texts of this

nature, have been selected with a view to stimulate interest and motivate thinking. In this way chemical principles and their applications are visualized by the student, thus adding to the clarity of text explanations.

From the above statements it should be evident that the text has been organized not only to aid the student, but also to assist the instructor in his teaching problems.

(2) **ASSIGNMENT:** Go over the main points covered in the assignment, emphasizing important parts, pointing out difficulties, and showing some of the practical applications.

(3) **TESTS:** Tests are conducive to study-habit formation. Have ready two mimeographed sheets, A and B, each containing a dozen or more questions of the one-word answer, the multiple-choice, or the matching-answer type. The tests should review the past class and laboratory work, and cover also the assignments of the day or week. Following the assignment, and previous to the lecture-recitation, give every alternate student the same set of questions. It will be evident that these tests will be a check of the student's review work, and the preparation for the advance assignment. Further checking is made possible by mid-semester and term examinations. After collecting the papers, immediately review the tests.

(4) **LECTURE, RECITATION, AND DEMONSTRATION:** Follow up the review of the tests by discussion of further points brought up in the assignment for the day or week. This may consist of lecture, informal questions, or discussion by the students. Lecture, accompanied by demonstrations and recitations, is an effective method for class work. The extent to which each of these different procedures is used will depend upon the lecturer and the size of the class, as well as the preparation and previous experience of the students.

## STUDY ASSIGNMENTS

Since textbook assignments depend upon the number of hours allotted to the course, and the previous training of entering students, the following assignments are suggested:

(1) For a *short course*, with all of the students having been carefully selected, the first eighteen chapters offer sufficient material for two hours of lecture-recitation and one laboratory period per week. This will constitute a *sixty-hour course*.

(2) For a *short course* when the time allotted for the course is the

same as in (1), but when all of the students have had the equivalent of a good course in high school or college chemistry, practically the entire text can be covered. This can be accomplished by reviewing the discussion part of the first eleven chapters (Inorganic) and selected parts of the laboratory exercises in the recitations and the laboratory assignments. Such a rearrangement will then allow these students extra class and laboratory periods for covering the organic section, and selected portions of the biological section. If pressed for time, the chapter on Blood and Lymph and the chapter on Hormones may be omitted as these subjects are treated in physiology. Also the chapter on Vitamins and Milk can be considered in nutrition. This then will constitute a sixty hour course.

(3) For a long course there is sufficient material in the twenty three chapters to cover one semester's work by assigning individual chapters, including the 'Suggested Activities'. Such a course will be suitable to schools of nursing which are affiliated with universities. It will constitute a ninety hour course.

## PART I

# INORGANIC CHEMISTRY

*The division of chemistry that deals with the study of lifeless or unorganized materials excepting those containing carbon, and includes the general principles underlying their transformations*

Technique for the administration of radioactive gold. Notice the heavy walled storage container from which the radioactive material is being removed. Courtesy Medical Division Oak Ridge Institute of Nuclear Studies Inc.



## SOME FUNDAMENTAL FACTS

## CHAPTER OUTLINE

## I CHEMICAL CHANGES

- (a) Analysis and synthesis
- (b) Factors influencing chemical change
- (c) Physiology correlation

## II MATTER AND ENERGY

- (a) Two states of energy
- (b) Chemical energy
  - (1) Its conservation
- (c) How chemical energy is measured
- (d) Energy value of foods

## III ELEMENTS AND THEIR OCCURRENCE

- (a) Elements the basic forms of matter
- (b) Metals and nonmetals
- (c) Importance of elements
  - (1) In the earth's crust
  - (2) In the human body

## IV COMPOUNDS AND MIXTURES

- (a) Compounds
  - (1) Law of definite composition
- (b) Mixtures
- (c) Pharmacology correlation

## I. CHEMICAL CHANGES

From remotest antiquity the thoughtful observer has been impressed by the fact that the different materials in nature about him are frequently undergoing *changes*. The burning of wood probably first attracted the attention of man as one of the greatest changes (Fig 1). As the original wood burns, heat and light are produced, and finally nothing visible remains but a few ashes. The rusting of metal, the souring of milk, the decaying of fruits and meats are further striking examples of these *chemical changes*. Foods undergo



Fig 1—Chemical Change. The campfire illustrates one of the best known chemical changes, i.e., burning. What are two main products of burning? Courtesy, H. Armstrong Roberts, Philadelphia



complicated chemical changes in the body. All processes for cooking involve chemical changes which not only make foods more palatable but also more digestible. The white of an egg, for example, is rendered more palatable by converting it into a soft white solid. *The study of changes in the composition of matter, and the energy transformations which accompany such changes, is the science of chemistry.*

## Analysis and Synthesis

If we apply fire to the wick of a candle we first observe that light is produced and then we notice heat is being generated. The candle is a poor medium for illumination because it produces more heat than light. Continued observation now informs us that the candle is disappearing.

If we hold a clean, dry inverted bottle over the burning candle, moisture will be seen to condense upon the inside of the bottle, which indicates that water ( $H_2O$ ) is being formed. The abbreviated writing of water as  $H_2O$  means that water is composed of two parts of hydrogen and one part of oxygen.

Now, if we lower the inverted bottle over the burning candle, the flame finally goes out. The invisible gas left in the bottle, if shaken up with some clear limewater, forms a milky white liquid. We know that we exhale carbon dioxide,  $CO_2$ , and this gas also gives this same test when by means of a glass tube we blow through limewater. We therefore conclude that carbon dioxide is also in the invisible gas formed when the candle burns. Further, we have been taught that oxygen in the air is necessary for breathing, and for the burning of any material, therefore if the oxygen in the  $H_2O$  and the  $CO_2$  came from the air, the candle must have been composed of hydrogen, H, and carbon, C, and perhaps oxygen O. By finding that the substance of the candle contains hydrogen and carbon we have illustrated a process called *analysis*.

The opposite of analysis, *i. e.*, the combining of substances to form a new substance, is called *synthesis*. Thus the combining of hydrogen and oxygen to form water is called the synthesis of water.

In all *chemical changes* the *composition* of the original substances has changed, and energy has been evolved or absorbed. If a change takes place wherein the composition is not altered (when you can still recognize the substance by some of its descriptive properties as the original substance with which you started), then the change is a *physical change*. No new substance is formed. In bending the arm, both physical and chemical changes take place (Fig. 2). In

the physical change, the voluntary muscle becomes harder, thicker, and shorter, while the cells are altered in size and position. The chemical change is primarily the result of the oxygen in the blood reacting with the sugar and fat. The proof of these chemical changes is evident in ordinary exercise. As the result of the in-



Fig. 2—Chemical Change in Muscles. In bending the arm both physical and chemical changes take place. What always is produced by a chemical change?

ternal and external work of the body, heat, a form of energy, is produced. Strenuous and prolonged exercise leads to an accumulation of lactic acid in the tissues, contributing to fatigue.

### Factors Influencing Chemical Change:

As the study of chemistry is continued it will be apparent that there are factors which promote chemical changes and affect their rates. *Heat, light and electricity*, all of which are forms of energy, are widely used for bringing about chemical changes. *Catalysts*, substances capable of changing the rates of chemical reactions without themselves undergoing any permanent chemical change, are important agents, and numerous examples of these will follow.

### Physiology Correlation:

What are the chemical changes producing muscle fatigue? What is derived from these chemical changes? Review the subject of fatigue, its causes and preventives. Chemically, why does eating sugar relieve fatigue? What have ventilation and perspiration to do with fatigue, and why is salt added to the drinking water of those whose labor produces profuse sweating?

### SELF-TESTING QUESTIONS

NOTE: At frequent intervals throughout the text, questions are inserted to serve as a quick checking device. If answered correctly they indicate

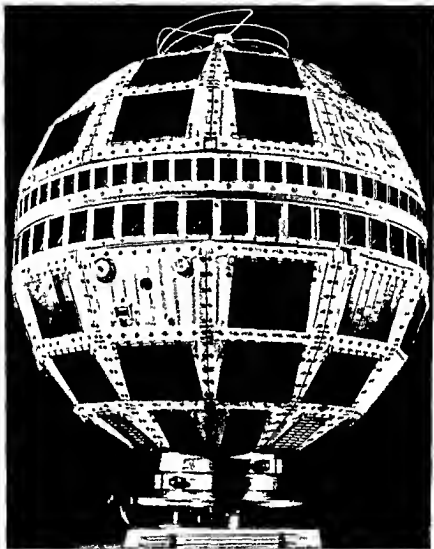


Fig. 3—The Telstar II Communications Satellite Built by Bell Telephone Laboratories. There are 3600 solar cells on its surface for transforming solar energy (light) into electrical energy. In what ways may satellites of this type prove useful to the medical profession? Courtesy, American Telephone and Telegraph Company

the mastery of the preceding section. Answers should be written out, whether or not the questions are assigned. They will serve later as a general review, prior to final tests.

- 1 What does the study of chemistry involve?
- 2 Define and give an example of analysis and of synthesis

- 3 What is the test for carbon dioxide?
- 4 What are three ways of recognizing a chemical change?
- 5 What three forms of energy may bring about chemical changes?

## II. MATTER AND ENERGY

In all chemical changes we deal first with *matter*, which is defined as anything occupying space and possessing weight, and second with changes which we call *energy* changes. By energy we mean the ability to do work, or to maintain motion in spite of opposing forces. Any form of matter—solid, liquid, or gas—possesses energy since it can always be placed in condition to do work. Fuels such as wood, gasoline, or gas possess energy since, when burned, they can do work by operating engines to produce motion. In fact, matter is energy in another form (Einstein). Familiar forms of energy are *light*, *heat*, *sound*, *electrical energy*, and *chemical energy*.

### Two States of Energy

In winding a clock spring, pumping water into an elevated reservoir, or lifting a heavy weight, work has been done and energy has been stored. This form of inactive energy which a system or group of bodies possesses by reason of position or configuration is called *potential energy*. Under changed conditions this energy can be released to do work. Potential energy can be transformed into energy of motion, which is called *kinetic energy*. This is the type of energy possessed by particles (molecules) moving at random (Fig. 4). In a hot body there is violent agitation and collision of the particles, while in a cool body they move more slowly. Energy of motion is usually dissipated as heat.

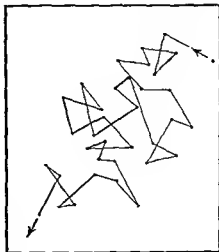


Fig. 4—Particles (Molecules) In Motion. The constant collision of minute moving particles (molecules) with other particles produces a motion in short, straight lines. Why do the particles have erratic motions?

## Chemical Energy:

Foods and fuels and all chemical substances possess potential energy which becomes available as heat or kinetic energy when chemical changes take place. Sometimes these energy changes become the most important part of a chemical reaction, and changes in the composition of matter are brought about with this end in view. For example, some of the food taken into the body is "burned" to give heat and mechanical energy, while some is used for building body structures. However, we burn fuels in a furnace to produce heat only. In this course we are particularly interested in the chemical energy stored up in foods. This results when energy from the sun (solar energy) is utilized by plants, through the agency of chlorophyll (klo'ro-fill), to synthesize carbohydrates, etc. Upon "burning" these foods in the body there is again released the same amount of energy which the sun supplied in producing the food. This energy is used primarily to keep the body at the normal temperature of 37° C. (98.6° F.), the necessary temperature for chemical changes which take place in it. Only a small amount of the energy from food is used to supply the body with mechanical energy, which is manifested by cell movement; most of it is used to keep the body at normal temperature. All experimental evidence points to the conclusion that energy can be transformed from one form to another without loss. These facts are usually expressed as the *Law of Conservation of Energy*, a law which states that *energy can neither be created nor destroyed, but may be transformed from one form to another.*

## How Chemical Energy Is Measured:

As chemical energy generally appears as heat energy we use heat-energy units to measure chemical energy. In the metric<sup>1</sup> system of measurement, the unit of heat energy is called a *calorie* (small), which is defined as the amount of heat required to raise the temperature of one gram of water one degree, centigrade.

In physics and chemistry the *calorie* (cal.) is used; but in nutritional studies the "*large calorie*," spelled with a capital *C* and

<sup>1</sup> The metric system of measurement is generally used in all scientific measurements. The unit of length is the *meter* (39.37 inches), which is divided into 100 centimeters. The unit of volume is the *liter* (1.05 quarts), which contains 1000 milliliters. The unit of weight is the *gram*, which is the weight of 1 milliliter of water at 4° centigrade. One liter of water weighs one kilogram (2.2 pounds). Remember—

1 meter	= 100 centimeters (cm) = 1000 millimeters (mm)
1 liter	= 1000 milliliters (ml), or cubic centimeters (cc.)
1 kilogram	= 1000 grams (Gm.)
1 gram	= weight of 1 ml. of water at 4° C.

equivalent to 1000 small calories, is the only one used. It is often called a *kilocalorie*. One of the best examples of a material containing chemical energy which can be transformed into heat energy is coal. When a man buys a ton of coal, he is interested in the amount of heat he has bought. By burning a sample of coal in a special apparatus, called a *calorimeter*, and by utilizing all of the heat generated to heat a weighed quantity of water, the number of heat units can be determined. In this country, fuel engineers generally use instead of the calorie a heat unit known as the British Thermal Unit (B.T.U.), and define it as the amount of heat required to raise the temperature of one pound of water 1° F. (See Fig. 1, p. 497.)

### Energy Value of Foods:

As previously indicated, the energy in foods has a certain caloric value as does coal. Sometimes, we are likely to overlook the fact that the foods we eat undergo chemical changes in the body with the formation of new living tissues. An outstanding illustration of this is shown by the fact that a baby's weight will ordinarily treble in a year's time. Also we are even more likely to overlook the great quantities of heat energy needed to keep the infant's body warm and supply it with energy for muscular activity. Much attention in the last few years has been given to the caloric value of foods as well as the influence of one food upon another during digestion. If the composition of a food is known, its approximate fuel value can be readily and easily determined. From observations of the amount of food consumed (dietary studies) it has been calculated that a man of average size, not engaged in physical labor, requires per day from his food approximately 2500 Calories of energy. Experiments have shown that one gram of fat taken as a food can produce nine Calories of heat, or enough heat to raise the temperature of 9000 grams of water 1° C. Fats contain approximately twice as much energy as either carbohydrates or proteins, as is shown below.

The table on page 10 shows the heat values of some foods. As a general rule the contents of numerical tables are not to be memo-

Class of Foods	Calories Per Gram	Calories Per Pound
Carbohydrates	4	1815
Fats	9	4082
Proteins	4	1815

nized but are to be examined carefully for facts of general interest and to be used for reference purposes

### FOOD VALUES

<i>Food</i>	<i>Protein Per Cent</i>	<i>Fat Per Cent</i>	<i>Carbohy- drates Per Cent</i>	<i>One Serving in Grams</i>	<i>Total Calories</i>
Bread	9.1	1.6	53.3	85	230.0
Butter	1.0	85.0		21	169.0
Beef (lean)	19.0	13.0		128	250.0
Bacon (smoked)	10.5	66.0		28	188.6
Eggs	13.4	10.6		106	179.0
Milk	3.3	4.0	5.0	170	123.6
Potato (baked)	3.3	0.3	22.7	210	245.0
Sugar			100.0	21	81.0

### SELF-TESTING QUESTIONS

- 6 With what two factors do chemical changes deal?
- 7 Define matter and energy
- 8 Name several different forms of energy
- 9 What is potential and kinetic energy?
- 10 What finally becomes of the energy of motion?
- 11 What are the two principal uses of energy produced in the body?
- 12 What is your explanation of the Law of Conservation of Energy?
- 13 Define the unit of heat energy in metric terms
- 14 Define the unit of heat energy in the British system

## III ELEMENTS AND THEIR OCCURRENCE

### Elements, the Basic Forms of Matter

In the study of foods and other chemical substances we find that all forms of matter are composed of one or more of 92\* *simple* or *elementary* substances which are considered as the basic forms of all matter. Sometimes these elementary substances or elements occur in the native or free state (uncombined) other times in a combined state. Thus iron sometimes occurs free in nature but it is found much more often in chemical combination with other elements for example with oxygen as the ore called *hematite*.

Many of the elements such as gold, silver, iron, and copper are familiar to us since they exist as solids. Ten of the elements are

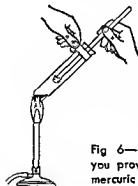
\*Eleven additional elements have been prepared artificially at this writing

gases, and two, mercury and bromine, are liquids at ordinary temperatures.

Of all elements, oxygen is the most abundant, but even so it escaped discovery until 1774, when Priestley, a chemist and minister, first prepared it by heating the red powder, mercuric oxide.



Fig. 5—Joseph Priestley. The discoverer of oxygen. Courtesy, "A Life of Joseph Priestley," Anne Holt (Oxford Press)



The gas evolved upon heating mercuric oxide causes a glowing splint to burst into flame and is called oxygen. During the heating a gray, silvery substance condenses on the inside of the test tube (Fig. 6). This substance is mercury.

Fig. 6—Mercuric oxide is readily decomposed by heat. How can you prove the presence of the elements, mercury and oxygen, in mercuric oxide?

Neither oxygen nor mercury has yet been decomposed into any simpler form by ordinary means. For this reason these two substances are called *elements* or elementary substances.

These simple substances (elements) are the units or "building blocks" out of which everything is made. Elements, however, may



chlorine, is a poisonous gas, yet the compound formed by the union of this element with sodium becomes a most important and valuable food material. In some cases, however, the most easily observable characteristics are the same before and after a chemical change. For instance, when the white solid, potassium chlorate, is heated, oxygen is evolved, and another white compound, potassium chloride, remains. A chemical change, however, has occurred. On the other hand, when ice is heated, its most obvious characteristics change. Still no change in chemical composition has taken place.

In the analysis of any sample of sodium chloride ( $\text{NaCl}$ ) one finds that the sodium and chlorine are always present in the same proportion by weight. In fact, in all salts and in all compounds, the elements present are united in a definite proportion by weight, i.e., the composition of a compound never varies. Any such established facts are called laws of nature, and this great generalization is known as the *Law of Definite Composition*, or as the *Law of Definite Proportion*.

### Mixtures, Substances of No Fixed Composition

Elements or compounds may often be mixed together without undergoing any chemical change and such a mixture may have its distinct ingredients present in a varying proportion, as are the ingredients in the soil, in the air, in the foods we eat, and in many medicinal preparations. Even though a mixture may appear to be homogeneous (the same throughout), by various methods it can always be shown that each component has retained its original characteristic properties and may be separated by some mechanical means. Iron powder, for example, can be separated from a mixture of powdered iron and sulfur by means of a magnet, or the sulfur can be dissolved in carbon disulfide, filtered away from the iron and recovered when the carbon disulfide evaporates.

The letters, the combinations of letters to make words, and the mixtures of separate letters and words to make a variety of sentences in this book illustrate the distinction made in chemistry between *elements*, *compounds*, and *mixtures*.

### Pharmacology Correlation

The importance of chemistry to *Materia Medica* is apparent when one consults the following partial list of the more important elements with some of their compounds. Note specifically the medicinal uses of these compounds and their action.

## SOME IMPORTANT ELEMENTS, THEIR COMPOUNDS AND USES

<i>Element</i>	<i>Compound of</i>	<i>Some Medicinal Uses</i>
Aluminum	Alum Aluminum acetate	Astringent to contract mucous membranes, as a gargle and douche Astringent and antiseptic in surgical dressings
Arsenic	Arsenic trioxide Potassium arsenite  Arsphenamine	Hematinic, <i>i. e.</i> , increases the amount of red corpuscles in the blood, thereby acting as a tonic to improve the appetite and digestion Specific for syphilis
Barium	Barium sulfate	Coats the stomach and intestines for taking x ray pictures
Bismuth	Bismuth subnitrate Bismuth subcarbonate	Insoluble compounds used as dusting powders on the skin, astringents and antiseptics for ulcerations of the stomach
Boron	Boric acid (boracic acid)	Mild antiseptic, nonirritating, particularly used for an eyewash
Bromine	Sodium and potassium bromides	Nerve sedatives
Calcium	Calcium chloride Calcium lactate	Assists in clotting of the blood. Calcium compounds are used for the treatment of tetany in children. Calcium salts are necessary for the growth of bones and teeth, for regulating muscular, nervous, and glandular activity.
Chlorine	Sodium chloride Chlorinated lime	Common salt Disinfectant for urinals and excreta. A deodorant
Copper	Copper sulfate (blue vitriol)	Removes granulations on the eyelids in trachoma. Produces vomiting. Used as an astringent.
Hydrogen	All acids, <i>e. g.</i> , hydrochloric  Hydrogen peroxide	Dilute solutions extract water from the tissues, and in the stomach aid digestion. Antiseptic
Iodine	Iodine tincture Potassium iodide	Antiseptic Treatment of syphilis, to increase secretions, and as treatment in hyperthyroidism

# SOME IMPORTANT ELEMENTS, THEIR COMPOUNDS AND USES

(Continued)

Element	Compound of	Some Medicinal Uses
Iron	Iron chloride	Hematinic as in cases of anemia Astringent
Lead	Lead acetate	Astringent Contracts tissues in ulcers and wounds
Magnesium	Magnesium citrate	Purgative
	Magnesium hydroxide (milk of magnesia)	Cathartic, neutralizes acidity of the stomach
	Magnesium sulfate (Epsom salt)	Purgative Allays inflammations
Mercury	Mercuric chloride (bichloride of mercury)	Local antiseptic
	Mercurous chloride (calomel)	Cathartic
	Mercuric salicylate	Intramuscular injection in syphilis
Nitrogen	Nitrous oxide (laughing gas)	Anesthetic
	Ammonia water	Cleanser, heart stimulant
Oxygen		Used in resuscitation in anoxia, and in basal metabolism
Phosphorus	Sodium phosphate	Saline purgative Reduces accumulation of fluid in the tissues, as in edema
Potassium	Potassium acetate	Diuretic
	Potassium permanganate	Antiseptic for wounds
	Potassium sodium tartrate	Saline purgative
Radium	Radium bromide	Treatment for cancer
Silver	Silver nitrate	Antiseptic to contract mucous membranes of eye, to cauterize, and for nose and throat inflammations
Sodium	Sodium bicarbonate (baking soda)	Acidosis treatment
Sulfur		Used in ointments for skin diseases. May be used as a laxative
Zinc	Zinc oxide	Astringent
	Zinc stearate	Dusting powder (irritating if inhaled)
	Zinc sulfate	Produces vomiting

**SELF-TESTING QUESTIONS**

- 18 How many elements are there?
- 19 Define a compound, and give several examples
- 20 What is the Law of Definite Composition? Explain it
- 21 How does a mixture differ from a compound?

**SUGGESTED ACTIVITIES****I THOUGHT PROVOKING QUESTIONS**

- 1 Besides a change in composition what is another evidence of chemical change?
- 2 When a candle burns is the matter being destroyed? Explain
- 3 Name several elements found in the body and state why they are important
- 4 By what ways can you distinguish between a compound and a mixture?
- 5 Do the following produce physical or chemical changes Dressing, breathing, eating, melting butter, souring of milk, decay of leaves, freezing of water, the formation of the crust on bread during baking, bandaging a wound?
- 6 Give five examples of chemical changes
- 7 In which of the three groups—elements, compounds or mixtures—does each of the following belong aluminum, milk soap, river water, ice cream face powder?
- 8 Why are we more familiar with iron than with silicon when silicon is much more abundant?
- 9 Calculate the approximate weight of iron in your body
- 10 Are most of the changes that occur in cooking, physical or chemical?
- 11 What characteristics differentiate the element from the compound?
- 12 Make a list of correlations between Chemistry and other nursing subjects, and give examples

**II VOCABULARY TESTING OF NEW TERMS**

The chemical words used in this and the following chapters are especially important to understand because you will be using them repeatedly in expressing your thoughts as you think in terms of chemistry

chemical change	kinetic energy	metal
chemical analysis	chemical energy	nonmetal
chemical synthesis	conservation of energy	compound
matter	calorie	definite composition
energy	calorimeter	mixture
potential energy	element	

**III TOPICS FOR ORAL OR WRITTEN REPORTS**

- 1 Phlogiston Theory
- 2 Philosopher's Stone

- 3 Discovery of Elements
- 4 Meaning of Names of Elements
- 5 The Caloric Value of Foods
- 6 Energy Requirements of the Body
- 7 Percentage of Elements in the Human Body

#### LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 640 642

**ATOMS, MOLECULES, AND THE ELECTRON THEORY****CHAPTER OUTLINE**

- |  |   |
|--|---|
| <b>I ATOMIC THEORY</b><br>(a) Molecules<br>(b) Atoms<br>(c) The atomic theory<br>(d) Atomic weight<br>(e) Symbols<br>(f) Formulas<br><br><b>II ELECTRON THEORY</b><br>(a) Structure of atoms<br>(b) Picturing the atom<br>(c) Isotopes<br><br><b>III VALENCE</b><br>(a) Meaning of valence | (b) Metals and nonmetals, chemical activity<br>(c) Valence of radicals<br><br><b>IV FORMULA WRITING</b><br>(a) Using valence to make formulas<br>(b) Structural formulas<br>(c) Practice in formula writing<br><br><b>V EQUATION WRITING</b><br>(a) Meaning of equations<br>(b) Balancing a chemical equation<br>(c) Practice in equation writing |
|--|---|

**I. ATOMIC THEORY****Molecules, the Physical or Structural Units of Matter:**

We know that most substances, iron, for example, expand when heated and contract when cooled, but that the weight of the substance does not change even though its volume has altered. Again, if we make a mixture of 50 ml of alcohol and 50 ml of water, we will have less than 100 ml. of the solution (Fig. 1). This smaller

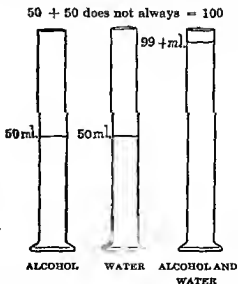


Fig 1—The mixture will not total 100 ml because of intermolecular displacement. Will this be true for all liquid mixtures?

combined volume is explained by saying that some of the particles of alcohol occupy spaces between particles of water, a condition which may be compared with the fact that one busbel of potatoes and one busbel of wheat, when mixed, do not fill a two busbel measure. From these and similar observations we may conclude that there are spaces between the particles of substances, not only between the particles of compounds, but also between the particles of elements. In the case of the element iron, the expansion in volume, due to the rise in temperature, means that the spaces between the particles of the iron have increased in size. These particles are in motion at all times and thus occupy a larger space when heated. *The smallest of these conceivable particles of matter (either elements or compounds) that can exist, take part in chemical reactions, and still be recognized as the original substances are called "molecules."* Molecules of the same particular substance are supposed to be alike in every respect.

From the foregoing statements it is evident that molecules are invisible particles which make up matter, and that the properties of matter are in reality the properties of the aggregate molecules.

### Atoms, the Chemical or Basic Structural Units of Elements

Imagine that a single molecule of water ( $H_2O$ ) is further divided. No longer will we have a molecule of water with all of its characteristic properties, but instead particles of hydrogen and oxygen from which the water molecule is constructed. These particles are *atoms*. Atoms rarely exist singly, but are almost always found in chemical combination with one another to form molecules. Molecules are sometimes the same particles as atoms *e g.*, atoms of

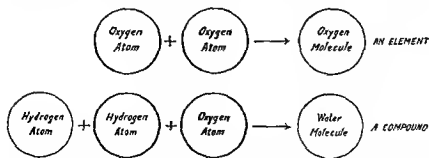


Fig. 2.—Difference Between a Gaseous Element and a Compound. How does the composition of a molecule of a gaseous element differ from that of a compound?

iron are identical with molecules of iron. Hence the iron molecule is monatomic.

Most metallic elements are like iron in that their molecules consist of but one atom. On the other hand, some of the active non-metallic elements, as oxygen and hydrogen, contain two atoms in each molecule, while other nonmetals, like phosphorus and arsenic, have even more atoms per molecule. Compounds like water ( $\text{H}_2\text{O}$ ), which are made up of different kinds of atoms, are also referred to as molecules. Hence there are elementary molecules, for example  $\text{O}_2$ , and compound molecules, for example  $\text{H}_2\text{O}$  (Fig. 2). Molecules usually are larger than atoms and are composed of atoms. *The smallest ordinarily\* indivisible part of an element is an atom.*

All atoms of the same element are alike in their chemical properties. When chemical changes occur between elements or compounds, it is between the atoms which constitute the reacting molecules. The properties of the resulting molecules are due to the separating, the rearranging, and the recombining of the atoms. The change is comparable to the tearing down of a building, separating the materials, and rearranging and combining these materials to form a new building with entirely new properties.

As has been stated, each molecule of an active gaseous element is made up of at least two atoms held together in chemical combination. In the case of compounds, as water,  $\text{H}_2\text{O}$ , two hydrogen atoms and one oxygen atom unite to form a molecule, and any amount of water is simply a collection of a definite number of these water molecules.

### The Atomic Theory:

In order to explain certain observed facts about chemical reactions, John Dalton, an Englishman, about 1807 formulated an atomic theory. This theory has never been replaced by a better one, but certain changes have been found necessary to keep it up to date. Some of these modifications in the theory will be discussed later. In brief, the original Dalton's atomic theory proposed

1. Chemical elements are made up of indivisible particles of matter called atoms.
2. All atoms of a given element are alike in physical and chemical properties.

\* It should be stated that certain substances called radioactive elements decompose spontaneously into other elements and that also by means of the cyclotron and other special machines nuclear changes in atoms can be brought about. The dream of the alchemists that is artificial transmutation of the elements has at long last been realized.



3. Atoms combine chemically in small whole-number ratios to form molecules.

Dalton's atomic theory has served as a cornerstone in the development of chemistry.

### Atomic Weights:

Atoms are so small that it is obviously impossible to weigh them individually. However, it is possible to weigh groups of atoms, each group containing the same number, and in this way to determine the *relative* weights of atoms in terms of a suitable reference standard. A carbon atom is taken as the standard for comparison, and assigned the value of exactly 12.000. This then makes the hydrogen atom, the lightest of all atoms, have a relative weight slightly greater than unity (1.00797). Scientists only recently changed over to carbon-12 ( $C^{12}$ ) as the reference standard. The  $C^{12}$  atom is the most abundant isotope of carbon (see page 27). The new atomic weight values, based on  $C^{12}$ , differ very little from those previously based on oxygen as exactly 16 000, since the two scales differ by only 37 parts in one million. On the new scale the atomic weight of oxygen becomes 15.9994. By making this change both chemists and physicists now have identical atomic weight scales.

Notice that the atomic weight of any element is the number which expresses the ratio of the weight of an atom of that element to one-twelfth the weight of the reference carbon atom. *Atomic weights are relative weights.* For example, the helium atom is

### SOME IMPORTANT ELEMENTS, THEIR SYMBOLS AND ATOMIC WEIGHTS BASED ON CARBON—12

<i>Element</i>	<i>Symbol</i>	<i>Atomic Wt</i>	<i>Element</i>	<i>Symbol</i>	<i>Atomic Wt</i>
Aluminum	Al	26 9815	Magnesium	Mg	24 312
Bismuth	Bi	208 980	Mercury	Hg	200 59
Bromine	Br	79 909	Nitrogen	N	14 0067
Calcium	Ca	40 08	Oxygen	O	15 9994
Chlorine	Cl	35.453	Phosphorus	P	30 9738
Copper	Cu	63 54	Potassium	K	39 102
Hydrogen	H	1 00797	Silver	Ag	107 870
Iodine	I	126 904	Sodium	Na	22 9898
Iron	Fe	55 847	Sulfur	S	32 064
Lead	Pb	207 19	Tin	Sn	118 69

approximately one-third as heavy as the reference carbon atom, and hence the atomic weight of helium is about 4.

Atomic weights of some of the more common and important elements are given in the table (p. 22). For the usual calculations requiring atomic weights it is permissible to approximate the values to the first place after the decimal.

### Symbols, Abbreviations for Elements:

Instead of writing out the names of elements it is often more convenient to use abbreviations. These abbreviations, called *symbols*, are usually the first letter or letters of the names of the elements, as H for hydrogen, O for oxygen, C for carbon, Ca for calcium, etc. To indicate more than one atom of the same kind write the proper figure in front of the symbol; thus 3 H represents three atoms of hydrogen. If, however, the atoms referred to form part of a molecule, then the number is written as a *subscript*, e.g.,  $H_2$  represents a molecule of hydrogen made of two atoms, and  $2 H_2$  represents two such molecules. All chemically active gaseous elements, when occurring alone, should be written to indicate their molecular condition, e.g.,  $H_2$  for hydrogen, and  $Cl_2$  for chlorine.

The symbol should also be remembered as representing not only an atom of the element, but also a definite weight, which, when expressed in grams, is called the "gram-atomic weight" of the element. For example, the hydrogen atom weighs 1.00797, and the oxygen atom weighs 15.9994. The symbol H then means 1.00797 grams of hydrogen, and the symbol O means 15.9994 grams of oxygen. Refer to page 631 for the names of the elements, their symbols, valences, and atomic weights.

### Formulas; Abbreviations for Compounds:

By the use of symbols we may represent the *composition* of a compound by indicating the *number* and the *variety* of atoms that make up its molecules, e. g.,  $H_2O$  represents one molecule of the compound, water, composed of two atoms of hydrogen and one of oxygen. Such an arrangement of symbols in representing a molecule is called the *formula* of that compound. In addition to telling at a glance what kind of atoms, and how many of them make up a molecule of a compound, the formula frequently informs us of the *nature* of the compound, and how it will be expected to behave. For instance, all acids are hydrogen compounds and the formula HCl not only shows the composition of the molecule, but also in this case

## SOME IMPORTANT FORMULAS

Hydrochloric acid	}	HCl	Calcium hydroxide	$\text{Ca(OH)}_2$
Hydrogen chloride			Sodium hydroxide	NaOH
Sulfuric acid	}	$\text{H}_2\text{SO}_4$	Magnesium sulfate	$\text{MgSO}_4$
Hydrogen sulfate			Mercuric chloride	$\text{HgCl}_2$
Carbonic acid	}	$\text{H}_2\text{CO}_3$	Potassium iodide	KI
Hydrogen carbonate			Potassium nitrate	$\text{KNO}_3$
Phosphoric acid	}	$\text{H}_3\text{PO}_4$	Sodium bicarbonate	$\text{NaHCO}_3$
Hydrogen phosphate			Sodium carbonate	$\text{Na}_2\text{CO}_3$
Nitric acid	}	$\text{HNO}_3$	Sodium chloride	NaCl
Hydrogen nitrate			Silver nitrate	$\text{AgNO}_3$

suggests the additional facts that it is an acid, will taste sour, and will show other characteristic properties of an acid. A formula also stands for a molecule of an element. For example, the formula for oxygen is  $\text{O}_2$ , showing that the oxygen molecule contains two atoms of oxygen.

A formula can also be used to represent a definite weight of a compound which, if expressed in grams, becomes the gram formula weight. For example, the gram formula weight of water ( $\text{H}_2\text{O}$ ) is 18.01534 grams. For most uses the value 18.0 is sufficient.

## SELF-TESTING QUESTIONS

1. Define and give an example of a molecule.
2. What is an atom?
3. How may the composition of a molecule of a metal differ from that of a nonmetal?
4. What is meant by atomic weight?
5. Define and give an example of a symbol.
6. What information does a formula convey?

## II. ELECTRON THEORY

During this present century there has been developed a theory called the *electron theory*, which explains the structure of the atom from an electrical standpoint. This new theory does not in any way overthrow former ideas as to the chemical union of atoms. It merely adds to older ideas, and clarifies what takes place in a chemical change.

## Structure of Atoms

According to the electron theory, the atom of every element (except ordinary hydrogen) is composed of positive electrical units called *protons*, negative electrical particles called *electrons*, and

neutral particles called *neutrons*. In any atom the number of electrons is equal to the number of protons, that is to say, under ordinary conditions the atom is electrically neutral. An electron is a very light particle, about  $1/1845$  of the weight of a hydrogen atom, the lightest of all atoms. In fact, the mass of the electron is so nearly zero that usually it is not considered in determining the total mass of an atom. On the other hand, the proton is heavier, and is approximately the mass of the hydrogen atom. Research has also shown the presence of a third kind of particle in the atoms of all elements excepting hydrogen. This third particle, called the *neutron*, is electrically neutral and has a mass nearly the same as the proton. Still other particles formed during "smashing" of atoms have been identified, but, for our purposes, discussion will be limited to the proton, electron, and neutron. Of these three different kinds of particles the free protons and the neutrons of an atom exist as a small dense mass in the nucleus, while the light electrons are far distant outside the nucleus, and revolve around the nucleus in various orbits much as the nine planets revolve around the sun.

Along with these discoveries there has been found a way to express the electrical charge of the nucleus of each of the various kinds of atoms. This electrical charge is called the *atomic number* and corresponds to the number of free protons (+ charges) in the nucleus or to the number of electrons (- charges) in the shells around the nucleus.

### Picturing the Atom

By means of the atomic number and the atomic weight (page 631) for each atom it now is possible to formulate some kind of a picture showing the differences in the structures of the various kinds of atoms.

Hydrogen, the lightest of all elements, has the simplest atomic structure since its atomic number is 1. The ordinary hydrogen atom contains just one proton and one electron (Fig. 3). There can be no neutron in its nucleus because the atomic weight of one agrees so closely with the weight of a proton.

The next simplest atom is helium with an atomic number of 2, and an atomic weight of 4. This atom, therefore, must contain two protons and two neutrons (symbol  $n$ ) in its nucleus, and two electrons revolving outside of the nucleus (Fig. 4). This completes the number of electrons possible in the first shell or energy level outside the nucleus of any atom.

The lithium atom with an atomic number of 3, and an atomic

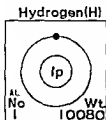


Fig 3—Hydrogen atom showing one electron rotating around one proton

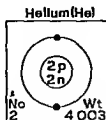


Fig 4—Helium an inactive element since its shell is complete

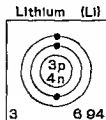


Fig 5—Lithium an active element containing one electron in its outer shell

weight of approximately 7, contains three protons and four neutrons in its nucleus and three electrons revolving outside the nucleus but since not more than two electrons can revolve in the first shell the third electron revolves in a second shell at still a greater distance from the nucleus (Fig 5) This second shell being larger, can hold as many as eight electrons before it is complete as may be noted by studying the structures of the seven elements (Figs 6 to 12)

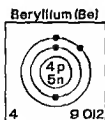


Fig 6

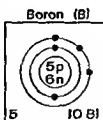


Fig 7

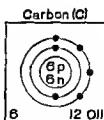


Fig 8

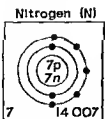


Fig 9

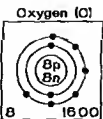


Fig 10

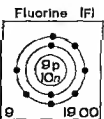
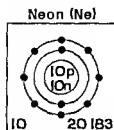


Fig 11

The above diagrams illustrate the conception of the structure of the atoms

Additional protons, with a corresponding increase in electrons, and an increase in neutrons, form combinations to give still heavier atoms. With successive elements the third shell builds up to eight electrons before a fourth shell is started. However, eventually with heavier atoms, the third shell builds to a maximum of eighteen electrons. The fourth shell may become stabilized with the number

Fig 12—Neon an inactive element with its electronic shell complete



8, 18, or 32, depending upon the mass of the atom. The element radium with its atomic number of 88 divides its electrons into consecutive shells as follows 2, 8, 18, 32, 18, 8, 2

### isotopes, Atoms of an Element Differing in Atomic Weight:

The mass of the electron is negligible when compared with the mass of the proton or the neutron. Since the mass of an atom depends almost entirely upon the number of nuclear protons and neutrons, each having essentially unit mass, it would seem that the atomic weight of any element should be a whole number. A glance, however, at the table of atomic weights shows that most atomic weights cannot be expressed by whole numbers. Lithium for example (Fig 13) with an atomic weight of 6.940 has two kinds of atoms. Both have an atomic number of 3, but one kind of atom has a mass of 6 (3 protons plus 3 neutrons), while the other kind has a mass of 7 (3 protons plus 4 neutrons). Ordinary lithium has both kinds of atoms, and consequently the atomic weight 6.940 represents a weighted average of the two different

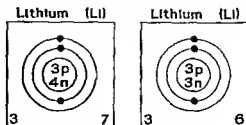


Fig 13—The two isotopes of lithium.

kinds of lithium atoms as they occur in natural lithium \* They differ only in the number of neutrons in the nucleus, and since both kinds of atoms have the same atomic number they are alike chemically These different forms of atoms of the same element, alike in most every respect except mass, are called *isotopes*

### SELF-TESTING QUESTIONS

- 7 What is the composition of an atom?
- 8 How can you distinguish between a proton an electron and a neutron?
- 9 How are the protons and electrons grouped in an atom? The neutrons?
- 10 What is the atomic number of an atom?
- 11 What are isotopes?

### III. VALENCE

#### Meaning of Valence:

A study of the formulas of the following compounds

HCl  
Hydrogen  
chloride

H<sub>2</sub>O  
Water

NH<sub>3</sub>  
Ammonia

CH<sub>4</sub>  
Methane

reveals the fact that different kinds of atoms are able to hold different numbers of hydrogen atoms in combination Recall that each hydrogen atom contains one electron in its shell The number of hydrogen atoms that will combine with (or replace) one atom of a given element is called the *valence* of that element Thus, in the previous formulas, *chlorine* (Cl) has a valence of one, *oxygen* (O) a valence of two, *nitrogen* (N) of three, and *carbon* (C) of four With the understanding of the established valence (combining power) of chlorine (1), of oxygen (2), nitrogen (3), and carbon (4) it is not difficult to reason that the valence of Fe in FeCl<sub>3</sub> is three, of Ca in CaO is two, of nitrogen in N<sub>2</sub>O<sub>3</sub> is three, and of Si in SiC is four

A theory has been worked out which explains valence in terms of the electrons in the outer shell of the atom In brief, the theory proposes (a) The valence of an element is equal to the number of electrons which an atom of that element must lose, gain, or share in order to realize a stable outer shell of electrons (b) When atoms attain stability by loss or gain of electrons they become charged particles, called ions The ions are then held together by electrical forces The structure which results is an ionic compound, and the type of valence is called *electrovalence*, or *ionic bonding* (c) Some atoms in their reactions gain stability for the outer shell by a

\*In Figs 3 through 12 the atomic weights given are for the elements in their natural occurrence and hence may express mixtures of isotopes.





stable number of eight electrons in its outermost shell. Notice that this has become possible by the sharing of two electrons, each atom contributing one for this purpose, hence these two electrons are the common property of both atoms. Since no electrons have been lost or gained by the chlorine atoms in arriving at the structure of the chlorine molecule, there are no ions present. Chlorine molecules are true molecular structures. The type of valence which arises from the sharing of electrons is covalence.



Fig. 15—Chlorine Molecule Covalence. Each atom shares an electron. Could molecules of some elements contain more than two atoms?

Many compounds are molecular in character. This includes not only numerous inorganic compounds, but also practically all organic compounds. The covalent type of bonding will be discussed later in more detail.

In summary, the following statements about the two types of valence are presented.

For ionic compounds

- (a) When stability of structure is attained by the loss and gain of electrons on the part of reacting atoms ionic compounds are produced.
- (b) The ion is a charged particle which has resulted from an atom gaining or losing one or more electrons in reacting.
- (c) The building units in the ionic type of compound are ions. In most cases ionic compounds are solid salts and metal oxides in which the ions have a definite geometrical pattern of arrangement.
- (d) The valence of an element which forms ionic compounds is equal to the number of electrons lost or gained by an atom of the element. Positive valence numbers are due to loss of electrons, and negative valence numbers are the result of a gain of electrons. Such valence, a characteristic of all ionic compounds is electrovalence.

For molecular compounds

- (a) In molecular compounds, stability of structure has been attained by the sharing of electrons on the part of the atoms involved.

- (b) In molecular compounds the molecule itself becomes the structural unit. Thus a given quantity of water is a collection of water molecules.
- (c) The valence of an element in a molecular compound is equal to the number of electrons which an atom of the element provides for sharing purposes. Often the valence numbers in molecular compounds are not represented by plus or minus inasmuch as no ions are present. This type of valence, which is characteristic of the atoms in true molecules, is covalence.

### **Metals and Nonmetals; Chemical Activity.**

Elements like sodium and calcium, which readily lose electrons, are generally solids, have a metallic luster, and are good conductors of heat and electricity. On the other hand, a number of the elements readily pick up electrons and do not have these physical properties.

The electron theory provides another way of classifying elements into metals and nonmetals. The metals are those elements that lose or tend to lose electrons in reacting and hence become electro positive, while the nonmetals are the elements which gain or tend to gain electrons and become electronegative. Certain elements have no pronounced tendency to gain or to lose electrons, and may behave either as nonmetals or metals, depending upon conditions of reaction. These are frequently called amphoteric elements. Those elements whose atoms tend to share electrons in reacting are usually viewed as nonmetals because the various atoms involved in the structure of the molecule become associated with a greater number of electrons.

Certain atoms in some cases may find it possible to lose only a part of the number of electrons which should be lost for ideal stability. Others may find that not all electrons needed for stability can be acquired, because of conditions of reaction. In such cases variable valence will be the result, however, every element has one valence that usually predominates. Copper, for example, has two valences, namely one and two, its valence of two is the more important.

Those elements whose atoms already have completed outer shells are inactive chemically, they cannot gain, lose or share electrons. Thus helium and neon (Figs 4 and 12) with completed outer shells are chemically inert and form no stable compounds.

### Valence of Radicals:

Frequently in life, groups of people cling together and act as a unit or part of a larger unit. So, in chemistry, associations composed of groups of atoms cling together, act as a unit, and have a definite valence. These groups of atoms are called *radicals* and have special names. For example, in the formula  $\text{H}_2\text{SO}_4$ , the one unit ( $\text{SO}_4$ ), called the sulfate radical, is combined with two atoms of hydrogen, and the valence is therefore two, or it is said to be divalent. If more than one of the radicals is used in making a formula, then the radical must be placed in parentheses and a subscript added, the subscript indicating that all of the atoms within the parentheses are to be taken a specified number of times. Thus, in the formula  $\text{Al}_2(\text{SO}_4)_3$ , three sulfate radicals are combined with two aluminum atoms. A radical is not a definite compound any more than the group of letters "ing" in "reducing" is a definite word; nevertheless, these groups of elements are essential in forming some compounds. Furthermore, in reactions in solutions, these radicals of the compounds usually remain unchanged as they move from one compound to another

### VALENCES OF SOME COMMON ELEMENTS AND RADICALS

Element or Radical	Symbol	Valence	Element or Radical	Symbol	Valence
Hydrogen	H	+1	Tin		
Sodium	Na	+1	Stannous	Sn	+2
Potassium	K	+1	Stannic	Sn	+4
Silver	Ag	+1	Aluminum	Al	+3
Barium	Ba	+2	Bismuth	Bi	+3
Magnesium	Mg	+2	Ammonium	$\text{NH}_4$	+1
Calcium	Ca	+2	Chlorine	Cl	-1
Zinc	Zn	+2	Bromine	Br	-1
Lead	Pb	+2	Iodine	I	-1
Copper			Oxygen	O	-2
Cuprous	Cu	+1	Sulfur	S	-2, +4, +6
Cupric	Cu	+2	Phosphorus	P	-3, +3, +5
Mercury			Nitrogen	N	-3, +3 to +5
Mercurous	Hg	+1	Carbon	C	-4
Mercuric	Hg	+2	Hydroxyl	OH	-1
Iron			Nitrate	$\text{NO}_3$	-1
Ferrous	Fe	+2	Bicarbonate	$\text{HCO}_3$	-1
Fenic	Fe	+3	Sulfate	$\text{SO}_4$	-2
			Carbonate	$\text{CO}_3$	-2
			Phosphate	$\text{PO}_4$	-3

The names, formulas, and valences of some of the more common elements and radicals are listed on p 32

### SELF-TESTING QUESTIONS

- 12 What is meant by valence?
- 13 What determines whether an element has a positive or a negative valence?
- 14 What are the two kinds of valence and to what is each due?
- 15 How does an ionic compound differ from a molecular compound?
- 16 What determines the activity of an element?
- 17 What is meant by a radical?
- 18 When the outer shell is complete is the element ordinarily active?

### IV. FORMULA WRITING

#### Using Valence to Make Formulas.

Sometimes it is necessary to make formulas for the compounds with which we are working. With an understanding of the meaning of valence and knowing the valences of elements and radicals, it is not difficult to write the formulas of most compounds. It should be kept in mind that the sum total of the valences of the positive elements or radicals must equal the sum of the valences of the negative elements or radicals in any compound.

Suppose that you wish to write the formula of calcium chloride. Then follow this procedure:

1 Write the symbols for the atoms in the compound, the positive acting atom being written to the left  $\text{CaCl}$

2 Mark the valences of the atoms above and to the right of their symbols. (When the compound is ionic, we generally do this by using as many plus or minus marks as equals the valence of the element or radical in the reaction and we use the sign that corresponds to the charge carried by the elements or radical in the particular reaction.)  $\text{Ca}^{++}\text{Cl}$

3 Find the least common multiple of the valences of the atoms or radicals (two in this example)

4 Divide the least common multiple by the valences of the two different atoms or radicals and use the numbers obtained as subscripts to indicate the ratio between the number of atoms in the compound



giving



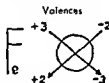
When the subscript is one (1), it is omitted and so whenever no subscript appears, it is understood to be one.

Notice that the number of atoms used is such as to give an equal number of positive and negative valences

The same method is used in making formulas with radicals, but a parenthesis is necessary when the compound radical is present more than once



An easy rule of thumb procedure for writing formulas is to "criss cross" valence numbers where odd and even valences are concerned



Sometimes an element may have more than one valence, that is, have a certain valence in one compound and a different valence in another. Whenever an element has two or more valences, the higher valences are usually represented by "ic" and the lower by "ous" in the names of its compounds. For example,  $\text{HgCl}_2$  in which mercury has a valence of two is mercuric chloride and  $\text{HgCl}$ , or  $\text{Hg}_2\text{Cl}_2$ , in which mercury has a valence of one is mercurous chloride while  $\text{FeCl}_3$  is ferric chloride and  $\text{FeCl}_2$  is ferrous chloride. A newer practice which is gaining in favor is to write mercury (II) chloride, mercury (I) chloride, etc., the Roman numeral in the parentheses showing the valence.

In some instances, such as in the case of  $\text{H}_2\text{O}_2$ , and  $\text{Fe}_3\text{O}_4$ , an element may have an unusual or even an apparently fractional valence, for reasons we need not consider.

### Structural or Graphic Formulas

Sometimes it is clearer to represent the valence by the use of a short line or a "bond" between the atoms. This provides a graphic representation of the arrangement of the atoms of elements in the molecules of compounds.

A study of the table on page 35 will illustrate structural formula writing.

Structural formula writing as a method of representing the relation of atoms to each other will become more apparent in the organic and biochemical discussions.

### Practice in Formula Writing

Making correct formulas for substances entering into a chemical change is so important that the chart on page 36 is inserted for practice. Combine each element or radical in the vertical column with

Elements	Valence	Formula	Structural Formula	Name of Compound
Hydrogen Chlorine	1 1	HCl	H—Cl	Hydrogen chloride
Hydrogen Oxygen	1 2	H <sub>2</sub> O	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{H} \end{array}$	Water
Hydrogen Nitrogen	1 3	NH <sub>3</sub>	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{N} - \text{H} \\ \diagup \\ \text{H} \end{array}$	Ammonia
Hydrogen Carbon	1 4	CH <sub>4</sub>	$\begin{array}{c} \text{H} \\   \\ \text{H} - \text{C} - \text{H} \\   \\ \text{H} \end{array}$	Methane (marsh gas)
Carbon Oxygen	4 2	CO <sub>2</sub>	$\begin{array}{c} \text{O} \\    \\ \text{C} \\    \\ \text{O} \end{array}$	Carbon dioxide
Nitrogen Oxygen	3 2	N <sub>2</sub> O <sub>3</sub>	$\begin{array}{c} \text{N} = \text{O} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{N} = \text{O} \end{array}$	Nitrogen trioxide

each element or radical in the horizontal column. Omit the squares in which an X appears

### SELF-TESTING QUESTIONS

- How can a simple formula of a compound be made by the least common multiple method?
- When an element has two or more valences how are they represented in the names of its compounds?
- What is meant by a structural formula?

	Chloride, Cl <sup>-</sup>	Oxide, O <sup>=</sup>	Sulfate, SO <sub>4</sub> <sup>=</sup>	Nitrate, NO <sub>3</sub> <sup>-</sup>	Carbonate, CO <sub>3</sub> <sup>=</sup>	Hydroxide OH <sup>-</sup>	Sulfide S <sup>=</sup>	Phosphate, PO <sub>4</sub> <sup>=</sup>
H <sup>+</sup> Hydrogen	HCl							
Ca <sup>++</sup> Calcium								
Na <sup>+</sup> Sodium								
Al <sup>+++</sup> Aluminum					X			
NH <sub>4</sub> <sup>+</sup> Ammonium		X						
Ag <sup>+</sup> Silver						X		
Fe <sup>+++</sup> Ferric					X		X	
Hg <sup>+</sup> Mercurous						X		
Zn <sup>++</sup> Zinc								
Mg <sup>++</sup> Magnesium								

## V. EQUATION WRITING

So far we have used the chemist's shorthand for writing the names of elements and compounds. Now we should go a step further and show how he denotes chemical changes, in a very brief way.

### Meaning of Equations:

With the help of symbols and formulas we can describe any chemical reaction by means of an *equation*. An equation, then, is simply a shorthand way of expressing a chemical reaction. The symbols and formulas of all materials undergoing change are placed on the left of the arrow, while the products formed are placed on the right. The arrow itself means "changes into," "yields," or "forms." For example, the union of iron and sulfur is expressed thus:

Word equations:

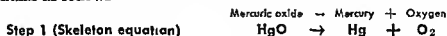
Equation with symbols and formulas

Iron plus Sulfur yields Iron sulfide  
 $\text{Fe} + \text{S} \rightarrow \text{FeS}$

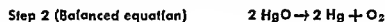
## Balancing a Chemical Equation

The mechanical features of simple equation writing require two steps

1 Write the correct formulas for the reacting substance or substances and the product or products formed. This might be called a *skeleton equation*. For example, in writing the equation to show what takes place when mercuric oxide is heated, write the correct formulas as follows



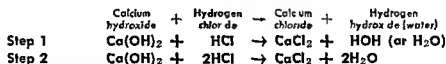
2 Balance the equation by prefixing such coefficients to substances as will make the same number and kind of atoms on each side of the arrow, *but under no consideration change a formula to make the atoms balance*



In forming compounds, keep in mind that the positive element or radical of one compound always unites with the negative element or radical of the second compound, and that the positive part of a compound is written first in the formula. Thus in the equation



the positive calcium unites with the negative chlorine and the hydrogen unites with the hydroxide radical. Thus we have



The gaseous elements must always be indicated in the molecular state, *e.g.*,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{N}_2$ , etc



Before attempting to write equations it should be pointed out that there is no one way of writing all chemical equations. Every one has to learn by practice the easiest way to write balanced equations for each particular type of reaction. Moreover, since the course of a chemical change *cannot* always be predicted it must be understood that *the chemical equation is an expression of experimental facts, and as such it cannot be altered*.



### Practice in Equation Writing:

Follow the two rules and find out whether you can write the correct formulas and balance the equations for the following reactions

- 1 Iron + Sulfur  $\rightarrow$  (use ferrous valence)
- 2 Carbon + Oxygen  $\rightarrow$
- 3 Phosphorus + Oxygen  $\rightarrow$  (use phosphorous valence)
- 4 Zinc + Hydrogen chloride  $\rightarrow$  (hydrogen liberated as gas)
- 5 Sodium hydroxide + Hydrogen chloride  $\rightarrow$
- 6 Silver nitrate + Sodium chloride  $\rightarrow$
- 7 Magnesium hydroxide + Hydrogen chloride  $\rightarrow$
- 8 Ammonium hydroxide + Hydrogen sulfate  $\rightarrow$
- 9 Magnesium chloride + Potassium carbonate  $\rightarrow$
- 10 Calcium hydroxide + Hydrogen carbonate  $\rightarrow$
- 11 Sodium chloride + Hydrogen sulfate  $\rightarrow$
- 12 Ferric chloride + Sodium hydroxide  $\rightarrow$
- 13 Aluminum oxide + Hydrogen chloride  $\rightarrow$
- 14 Mercurous nitrate + Ammonium chloride  $\rightarrow$
- 15 Sodium sulfide + Mercuric chloride  $\rightarrow$
- 16 Calcium hydroxide + Hydrogen phosphate  $\rightarrow$
- 17 Ferrous nitrate + Ammonium sulfide  $\rightarrow$
- 18 Zinc carbonate + Hydrogen phosphate  $\rightarrow$
- 19 Copper sulfate + Ammonium hydroxide  $\rightarrow$  (use cupric valence)
- 20 Aluminum sulfate + Sodium carbonate  $\rightarrow$

### SELF-TESTING QUESTIONS

- 22 What does an equation show?
- 23 What two steps are followed in writing a chemical equation?
- 24 Why must you never change a formula to make atoms balance?
- 25 How are active gaseous elements written?

### SUGGESTED ACTIVITIES

#### I THOUGHT PROVOKING QUESTIONS

- 1 When is a chemical change completed?
- 2 Why are some elements more active than others?
- 3 What part of an atom determines the activity of an element?
- 4 What are the valences of the positive elements in the following compounds  $\text{HgCl}$ ,  $\text{HgCl}_2$ ,  $\text{ZnSO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{AgNO}_3$ ,  $\text{MgO}$ ,  $\text{Ca}(\text{HCO}_3)_2$ ?
- 5 When is a formula written without subscripts?
- 6 When do certain elements have a zero valence?
- 7 What should be known before a chemical equation is written?
- 8 When an equation will not balance, what should be the first thing checked?
- 9 Why may coefficients, but not subscripts be changed while balancing an equation?

- 10 Which of these equations are unbalanced or incorrectly written?
- $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + 2\text{H}$
  - $2\text{KClO}_3 \xrightarrow{\text{heat}} 2\text{KCl} + 2\text{O}_2$
  - $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$
  - $\text{Mg}_2 + \text{N}_2 \rightarrow \text{Mg}_2\text{N}_2$
  - $\text{CuO} + 2\text{H} \rightarrow \text{Cu} + \text{H}_2\text{O}$
- 11 What does the formula of a compound stand for?
- 12 Make a diagram of the calcium atom, considering it to have an atomic number of 20 and an atomic weight of 40
- 13 How do you account for the fact that the atom of heavy hydrogen (deuterium) has an atomic weight of 2?
- 14 What is meant by a 'weighted average'?
- 15 In what ways has the original Dalton's atomic theory been modified?

## II VOCABULARY TESTING OF NEW TERMS

molecule	formula	valence electrons	amphoteric
atom	atomic number	valence	radical
atomic weight	proton	metal	structural formula
symbol	electron	nonmetal	variable valence

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- The Electron Theory
- Within the Atom—Atomic Structure
- Why Formulas and Equations Have Value
- The Change to Carbon 12 for Relative Atomic Weights

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 644, 646, 648

# OXYGEN—THE LIFE-SUPPORTING ELEMENT

## CHAPTER OUTLINE

- |  |   |
|--|---|
| <b>I IMPORTANCE AND ABUNDANCE</b><br>(a) Importance<br>(b) Abundance   | <b>III FIRES</b><br>(a) Matches<br>(b) Fireproof materials<br>(c) Fire extinguishers  |
| <b>II PREPARATION AND PROPERTIES.</b><br>(a) Preparation<br>(b) Properties<br>(c) Oxides<br>(d) Oxygenation<br>(e) Oxygenating agents<br>(f) Combustion<br>(g) Oxidation and combustion<br>(h) Oxidation and reduction from the electronic view<br>(i) Spontaneous combustion<br>(j) Another form of oxygen<br>(k) Uses of ozone | <b>IV USES OF OXYGEN</b><br>(a) Oxygen in nature<br>(b) Oxygen in industry<br>(c) Oxygen in medical practice<br>(d) Air conditioning<br><br><b>V PHYSIOLOGICAL CORRELATIONS</b><br>(a) Respiration<br>(1) Oxygen in breathing<br>(2) Oxygen in medicine<br>(b) Oxygen requirement<br>(c) Symptoms of anoxemia<br>(d) Guide for oxygen therapy |



Fig 1—Infant incubator New techniques in obstetrics and pediatrics have been major factors in lengthening the life expectancy of the children born today In what other ways has chemistry contributed to an advance in life expectancy? Courtesy, New York Life Insurance Company

## I. IMPORTANCE AND ABUNDANCE OF OXYGEN

### Importance:

It is difficult to realize just how much we depend upon the free oxygen of the air. Every breath of life consumes some of this gas. Man can live without water for a few days and without food for weeks, but lack of oxygen, the most fundamental requisite for maintenance of life, is fatal within a few minutes. Not an animal and scarcely a plant can live without it, and a fire cannot be started without it to produce heat and light. Oxygen is the one element that is essential in bringing about, through chemical changes, the conversion of the chemical energy of foods and tissues into heat and mechanical energy, the latter being used in producing body movement and activity of the organs and tissues. Only a small part of the food eaten is used to repair or build tissues. The important place of oxygen in the industrial world is discussed later in this chapter.

### Abundance:

We live in a vast ocean of air, of which about one-fifth consists of free molecular oxygen. In the combined state, oxygen is even more widely distributed. It makes up eight-ninths, by weight, of all the waters of the earth, almost one-half of the earth's crust, two-thirds of our bodies, and a large part of all vegetable matter.

#### COMPOSITION OF THE ATMOSPHERE (DRY)

Component	Percent by Volume	Formula
Nitrogen	78.04	$N_2$
Oxygen	20.93	$O_2$
Argon	0.94	Ar
Other gases	0.04	

Because of its great importance and abundance oxygen is the natural element with which to begin the systematic study of typical chemical changes of the elements and their more important compounds.

#### SELF-TESTING QUESTIONS

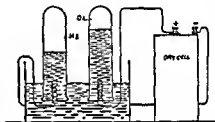
1. Why is oxygen considered the most important element in our lives?
2. Where is oxygen the most abundant in the free state? In the combined state?
3. Which element is the most abundant component of the atmosphere?

## II. PREPARATION AND PROPERTIES

### Preparation:

For commercial purposes a cheap and abundant supply of oxygen is usually obtained by evaporating the more volatile nitrogen from liquefied air. Oxygen may also be obtained, along with hydrogen, by decomposing water with electricity. This latter process is called *electrolysis* (Fig. 2). It is rather difficult to separate absolutely pure oxygen from the other gases in the atmosphere; therefore in the laboratory it is usually prepared by liberating it from some of its compounds. A convenient and common laboratory method of

Fig. 2—Decomposing Water. Electrolysis of water ( $H_2O$ ) forming two volumes of hydrogen and one volume of oxygen. How can you prove that the collected gases are hydrogen and oxygen?



obtaining oxygen is to heat potassium chlorate, a compound of potassium, chlorine, and oxygen. The chemical change in this case is represented as follows:



The ending "ate," as used in the compound "potassium chlorate," signifies a compound composed of three elements, of which oxygen is one. The ending, "ide," as in *potassium chloride*, is used for all compounds composed of two elements.

In the laboratory method of preparation it is customary to mix with the potassium chlorate some manganese dioxide. This causes the reaction to take place readily at a lower temperature than is otherwise possible.

A material like manganese dioxide, the influence of which either hastens or retards the speed of a chemical reaction, without being altered itself, is called a *catalytic agent* or simply a *catalyst*. In our study of many chemical reactions catalyzers will demand frequent attention. The action of a catalytic agent is comparable to a fore-

man of a group of men whose mere presence greatly improves the performance of the workers.

### Properties

Pure oxygen is a colorless, odorless, tasteless gas, slightly soluble in water. The most noticeable and important chemical property of oxygen is its ability to combine directly with many other elements, especially at high temperatures.

### Oxides

Almost all of the elements (metals and nonmetals) combine with oxygen to form a large class of compounds which are called *oxides*. Also many compounds already containing oxygen may unite with more oxygen, e.g., carbon monoxide (CO) to form carbon dioxide (CO<sub>2</sub>), and sulfur dioxide (SO<sub>2</sub>) to form sulfur trioxide (SO<sub>3</sub>).

#### OXIDES

<i>Metallic Oxides</i>		<i>Nonmetallic Oxides</i>	
Sodium oxide	Na <sub>2</sub> O	Carbon dioxide	CO <sub>2</sub>
Calcium oxide	CaO	Chlorine monoxide	Cl <sub>2</sub> O
Magnesium oxide	MgO	Nitrogen trioxide	N <sub>2</sub> O <sub>3</sub>
Bismuth oxide	Bi <sub>2</sub> O <sub>3</sub>	Phosphorus pentoxide	P <sub>2</sub> O <sub>5</sub>
Cupric oxide	CuO	Sulfur dioxide	SO <sub>2</sub>

Some naturally occurring oxides are water (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), sand (SiO<sub>2</sub>), and hematite (Fe<sub>2</sub>O<sub>3</sub>). Notice that an *oxide* is a compound of oxygen with but one other element, and hence it is a *binary* compound. The oxides form a highly important group of compounds, one of the four large classes in inorganic compounds—*oxides, acids, bases, and salts*.

### Oxygenation

The actual process of a substance uniting with oxygen is called *oxygenation*. The union may be rapid or slow, and is so slow in some instances that it is hardly perceptible that any change is taking place. Common examples of this slow oxygenation are the rusting of iron in the presence of moisture (Fig. 3), the decay of plant and animal matter, or the oxygenation of food materials in the body during respiration (*breathing*). It is by means of this slow

oxygenation of foods that the body temperature is kept constant and slightly higher than that of the surroundings. The body tissues are oxygenated only when worn out and dead, and even then the heat produced is negligible. Certain catalytic agents called *enzymes* (en'zims), in both animal and vegetable tissues, permit oxygenation at comparatively low temperatures of foods, tissues, and many substances found in the cells. In fact, it is oxygenation that produces the energy for maintaining body temperature, muscular contraction, glandular secretion, and nerve impulses. Another example of oxygenation which is of special interest and importance to the nurse is the destruction of certain disease-producing bacteria by free oxygen or by compounds which contain oxygen.



Fig. 3—Slow Oxygenation. An iron pipe destroyed by rusting or slow oxygenation. How can iron be protected from oxygenation? Courtesy, New Jersey Zinc Co.

### Oxygenating Agents (Oxidants):

Three medicinal compounds parting with their oxygen readily and therefore used as oxygenating agents (oxidizing agents, oxidants) are the germicides hydrogen peroxide, potassium permanganate, and sodium hypochlorite. Anaerobic bacteria, as tetanus bacilli, cannot live in the presence of free oxygen, and consequently wounds infected with this kind of bacteria are kept open so that these organisms may be oxygenated and killed.

### Cambustion:

When oxygenation takes place rapidly enough to produce light as well as heat, the process is called burning or combustion. In a



Fig 4—Rapid Oxygenation The cause of this is believed to be a grain dust explosion Which of the factors determining the rate of oxygenation is responsible for this fire? Courtesy, National Board of Fire Underwriters

broad sense, *any energetic chemical combination accompanied by light* is also known as burning or combustion whether oxygen is involved or not. Whether oxygenation is rapid or slow, provided that the same products are formed, the amount of energy produced is the same. The rate at which oxygenation takes place is governed by four conditions: (1) *the nature of the materials* undergoing oxygenation, *e.g.*, wood as compared to coal; (2) *the temperature* of the material being oxygenated; *respiration*, for instance, is more rapid in warm blooded animals; (3) *the concentration of the oxygen* which surrounds the materials undergoing oxygenation; and (4) *the extent of exposed surface, i.e.*, the greater the surface exposed the more rapid is the oxygenation.

Not only the rate of an oxygenation process, but the rates of all chemical reactions in general, are determined by the above four factors



### Oxidation and Combustion:

The combination of oxygen with an element produces a rise in the valence of the element. Thus, when metallic magnesium combines with oxygen, its valence is raised from zero to two ( $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ ). Similarly, the oxygenation of a compound always implies a rise in the valence of one or more of the elements in the compound ( $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ). Now, other elements besides oxygen can raise the valence of another element either in the free state or in combination. Thus, when sulfur combines with magnesium to form magnesium sulfide ( $\text{Mg} + \text{S} \rightarrow \text{MgS}$ ) the valence of the magnesium is raised from zero to positive two. This process in which the positive valence of an element which is either in the elementary state or in a compound is raised, whether through the action of oxygen or of some other substance, is known as *oxidation*. The element or compound on which this change is wrought is then said to be *oxidized*, and the agent which brought about the oxidation is known as the *oxidizing agent* (oxidant). Oxygenation reactions are, therefore, oxidation reactions at the same time, but in addition there are many oxidation reactions which do not involve oxygen and are therefore not oxygenation reactions.

The reverse process to oxidation is *reduction*. Reduction is the process in which the positive valence of an element is lowered, the agent producing the lowering being known as a *reducing agent* (reductant). In the case above of the combination of sulfur and magnesium, the valence of the sulfur is lowered from zero to negative two, hence in this case the sulfur is reduced.

### Oxidation and Reduction from the Electronic View:

It will be remembered from the discussion of the electron theory that, in some reactions, when combination of substances takes place, electrons are transferred from the atoms of some elements to the atoms of others. The valence of an element is considered to be zero in its free state; if the valence of an element is increased, its atoms give up some electrons, while if the valence of an element is lowered, its atoms receive some electrons. For example, when magnesium combines with oxygen to form magnesium oxide, each magnesium atom transfers two of its electrons to the oxygen atom with which it combines. Similarly, when magnesium and sulfur combine, each magnesium atom transfers two of its electrons to the sulfur atom with which it combines. The following diagram illustrates the valence changes (transfer of electrons).

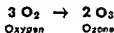


### Spontaneous Combustion:

Frequently the heat produced by oxidation cannot escape, particularly when the material undergoing oxygenation is a poor conductor of heat. At such times the temperature of the substance will gradually rise as oxidation progresses. This rise in temperature further increases the rate of oxidation and soon a temperature is reached at which the material bursts into a flame. This temperature is called the *kindling temperature* and the materials are said to have caught fire by *spontaneous combustion*. Oily rags left by painters, slack coal in the closed hold of a ship, sawdust heaps, and damp fermenting hay in stacks are materials which often take fire because of spontaneous combustion. Nondrying oils such as mineral oils do not undergo spontaneous combustion, but they are combustible.

### Another Form of Oxygen

Frequently during lightning discharges, or during the operation of x ray machines, or other electrical apparatus, which produce an electrical discharge through air, the oxygen absorbs electrical energy and is converted into a form of oxygen called "ozone" ( $O_3$ ), which may be recognized by its peculiar pungent odor. In this change three volumes of oxygen are changed into two volumes of ozone



### Uses of Ozone

Ozone is an active oxidizing agent and is very effective as a deodorizer and disinfectant, but even though it does remove odors and kill germs, it has not been of much practical use in purifying air or water. Instead of using ozone for water purification chlorine usually is used, since chlorine is not only more effective but also cheaper. In our own country ozone has been used to some extent in bleaching oils, waxes, flour, and starch. Ozone is seldom in high enough concentration to kill the bacteria of the air, and along with its irritating effect on the lungs, is not to be considered as an effective disinfectant for air in hospitals or rooms. Although there are only traces of ozone in the air near the earth, because it reacts with the ever present water vapor to form hydrogen peroxide ( $H_2O_2$ ), its presence in larger quantities at higher altitudes is important since ozone has the power to absorb some of the ultraviolet rays from the sun and thereby prevent these radiant rays from causing fatal sunburns and blindness. However, a small amount of these

rays reach animal life and are instrumental in preventing the bone disease known as "rickets." Ozone is very similar to oxygen in its properties, but it is very much more active because of its greater energy content. Such different forms of the same element, as oxygen and ozone, which differ somewhat in their properties but chiefly in their energy content, are said to be *allotropic forms*. Phosphorus, sulfur, and carbon are other elements which have allotropic forms.

### SELF-TESTING QUESTIONS

- 4 By what two commercial methods is oxygen obtained?
- 5 Define and give one example of electrolysis catalytic agent oxide, oxidation combustion enzyme, oxidizing agent spontaneous combustion kindling temperature
- 6 Name three medicinal oxidizing agents
- 7 What is ozone and what are its uses?

### III. FIRES

Since oxygen is associated with burning, which may be helpful or destructive, a brief discussion of fires and methods for extinguishing them is needed. In hospitals, rest homes, and similar institutions, where many of the patients are bedfast and practically helpless, fire prevention measures assume added importance. Personnel must be adequately trained in prevention of fire, and in procedures for combating fire quickly and effectively.

#### Matches:

The "strike anywhere" or *friction* match tips are often composed of phosphorus sulfide, potassium chlorate, and paraffin. When the match is rubbed over a rough surface, the heat of friction raises the phosphorus sulfide to its kindling temperature. The potassium chlorate or some other oxidizing agent furnishes sufficient oxygen to make the combustion more rapid. Enough heat is generated to cause first the paraffin and then the wood to burst into a flame and burn. Because of fire hazards the strike anywhere match, once known as the "parlor match," has been to some extent replaced by the *safety match*. The head of this match contains antimony sulfide, a compound that is more difficult to ignite by friction than phosphorus sulfide. The antimony sulfide is mixed with a suitable oxidizing agent, and the combination is held together with glue. One side of the match box has been coated with a mixture of

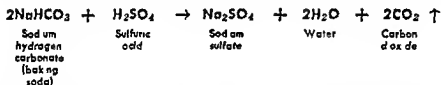
powdered glass and red phosphorus, the red phosphorus being an aid in the ignition of the antimony sulfide. Such a match is seldom ignited accidentally.

### Fireproof Materials:

When a substance does not combine with oxygen it cannot burn, and it is then said to be "fireproof." Fireproof materials either do not combine with oxygen, except at high temperatures, or they already are completely oxidized. Asbestos and granite are well known examples of substances which cannot burn, they are the products of combustion formed by nature long ago. If clothing, wood, or any absorbent material is coated or saturated with certain oxides, or other incombustible compounds, the material then becomes fire resistant.

### Fire Extinguishers

Most chemical fire extinguishers contain some liquid which surrounds and often cools the burning fuel with a noncombustible gas. A common type of extinguisher uses water and carbon dioxide. In the soda acid type, the carbon dioxide is generated as follows:



The water forced out by the carbon dioxide cools and smothers the flame, much as would a wet blanket. In the clear water type, carbon dioxide in liquid form is contained in a sealed cartridge suspended in water. Both types, upon inversion of the extinguisher, pressurize the container and expel the water. A more recent type of fire extinguisher is essentially a portable steel tank which is *charged with liquid carbon dioxide under pressure*. Upon opening the valve the liquid carbon dioxide quickly evaporates and escapes as a cloud through a funnel shaped nozzle which can be directed on the fire (see Fig. 6, page 208).

Liquid fuels, like burning oil or gasoline which are lighter than water, do not mix with it and therefore float on top, and are best smothered without the use of water. It is for this reason that, in addition to the usual types of extinguishers, sand or a blanket is often kept in chemical laboratories to smother a fire.

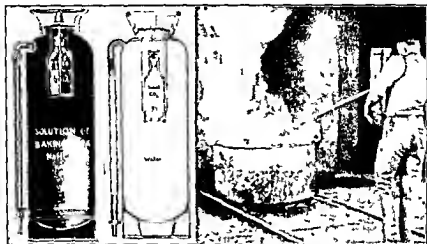


Fig 6—Smothering a Fire Hospitals usually have one of the above types of fire extinguishers available in the corridors for an emergency fire. What is the position of the extinguisher when in use? Courtesy, Walter Kiddle & Company, Inc.

Foamite, a highly effective commercial fire extinguisher for use on burning oil or gasoline, contains aluminum sulfate in place of sulfuric acid, and in addition has a licorice extract which aids in forming a thick, tough foam filled with carbon dioxide bubbles. This foam acts as a blanket in excluding the oxygen. The light, insoluble solid, aluminum hydroxide, produced according to the following equation, makes the foam more durable:



It is interesting that this reaction is similar to that of an alum baking powder. A small portable fire extinguisher suitable for the home is the pyrene fire extinguisher (p 277), which contains liquid carbon tetrachloride. This liquid, when sprayed on a fire, volatilizes and surrounds the flame with a noncombustible gas to the exclusion of oxygen.

### SELF-TESTING QUESTIONS

- 8 What materials are used in making a "strike-anywhere" match?
- 9 How does a safety match differ in composition from a "strike anywhere"?
10. Why is a safety match considered to be safe?
11. When is a substance fireproof?
12. How is absorbent material made fireproof?
- 13 What is the principle of the carbon dioxide fire extinguisher? Of the Foamite fire extinguisher? Of the pyrene fire extinguisher?



Fig. 7—Extinguishing Fire with Dry Chemical. This new type of extinguisher expels dry powder to coat over burning material. Why would this be effective? Courtesy of Fyr-Fyter Company

#### IV. USES OF OXYGEN

##### Oxygen in Nature:

Oxygen is an important constituent of the majority of the compounds in the earth and of the creatures on it. Most forms of animal life need oxygen to live. Land animals receive their oxygen from the air, while many aquatic animals obtain their oxygen from the air dissolved in the water. The oxygen in the air aids in reducing the refuse organic matter by a process called decay, which is further hastened by bacteria. In this way the earth is freed from a surface accumulation of dead plant and animal products, and in

a similar way natural water is freed from pollution. It is the oxygen dissolved in water that is so important in the disposal of sewage. For this reason the sewage is mixed with a large volume of water so that large quantities of dissolved oxygen will be available for oxidation purposes. Although oxygen serves a very useful purpose in producing decay, as in the case of dead plants and animals, still it is detrimental to the keeping of foods. As a consequence various ways are used to prevent this action such as refrigeration, cooking, canning, salting, drying, freezing, and smoking. Oxygen, too, constantly eats away metal surfaces and the rust and corrosion that result represent millions of dollars in waste annually.

### Oxygen in Industry

An important industrial use of oxygen is to produce high temperatures, as in the oxyhydrogen and oxyacetylene flames for welding metals, making repairs on machinery and cutting iron. The oxyacetylene flame gives a temperature as high as  $3500^{\circ}\text{C}$ . In cutting iron the oxyacetylene flame heats the iron and then with most of the acetylene cut off, the compressed oxygen rapidly burns away the iron. Cylinders of commercial oxygen for the above purposes are familiar objects in automobile service stations. In recent years the steel industry has been using increasing quantities of oxygen to operate furnaces.

### Oxygen in Medical Practice

The therapeutic uses of oxygen in impeded respiration (pneumonia), in treatment of poisonous vapors as nitric acid fumes and in conjunction with anesthesia are discussed under Physiological Correlations (p. 55).

### Air Conditioning

For years ventilation has been the only means of supplying us with healthful air. Investigation has shown that the injurious effects of bad ventilation are not so much due to a low percentage of oxygen or an excess of carbon dioxide in the air but rather to high temperature, an abnormal amount of water vapor (humidity), and poor circulation of air.

A closed area containing many people does not provide adequate ventilation. There is nothing quite so uncomfortable as the lack of ventilation, and for that reason many hospitals, dwellings, public



buildings, and transportation devices such as trains, airplanes, and automobiles have established intricate systems to provide proper air conditions. Air conditioning is the simultaneous control of (a) temperature, (b) humidity, and (c) air movement. These three factors must maintain a definite relationship to each other in order to insure bodily comfort. We warm or cool our rooms just enough so that the body loses heat at a comfortable rate. The body gets rid of its surplus heat by radiation and conduction to the surrounding air, and by evaporating moisture at the surface of the body. A high temperature decreases the rate at which the body can lose its heat by direct conduction, while a high humidity decreases the rate at which moisture can evaporate. Low temperature produces opposite effects. Evidently then the *ill effects of bad ventilation are the result of interference with heat regulation of the body*. The air movement is necessary to maintain an adequate supply of fresh air, otherwise the body breathes expired air, saturated with moisture at body temperature, and consequently very little heat can be eliminated by radiation, conduction, and evaporation. When any one of these three factors is out of proportion the body becomes uncomfortable. It is air conditioning which regulates and maintains these proper conditions.

### SELF-TESTING QUESTIONS

- 14 How does oxygen purify the land?
- 15 What are the chief industrial uses of oxygen?
- 16 What is air conditioning?
- 17 What factors are considered in air conditioning?

## V. PHYSIOLOGICAL CORRELATIONS

### Respiration:

**OXYGEN IN BREATHING** Oxygen combines loosely with the hemoglobin, the respiratory pigment in the red corpuscles of the blood. There is also a little oxygen dissolved in the blood. Taken together the combined oxygen and the dissolved oxygen make nearly as high a percentage of oxygen in the blood as in the air. Hemoglobin, combined with oxygen, is bright red (arterial blood flowing from the lungs), but after giving up its oxygen to the blood capillaries it is a deep bluish purple (venous blood). This is the reason for the different color of blood flowing from arteries and from the veins.

The oxygen circulates through the tissues in all parts of the body,

oxidizing the sugars, fats, all broken down material, and certain poisonous substances, with the formation of heat, lactic acid, carbon dioxide, and water. The speed of the oxidation is influenced by enzymes called *oxidases*, which act as *catalyzers*. The water is eliminated by the kidneys, sweat glands, and lungs. The carbon dioxide is carried by the blood to the lungs and then exhaled. A



Fig. 8—The Breath of Life. Oxygen mixed with a small amount of carbon dioxide as a respiratory stimulant is being used in reviving a newborn baby. Courtesy, Ohio Chemical and Mfg Co

considerable amount of the lactic acid is converted into a carbohydrate called glycogen which is then deposited in muscle tissue and in the liver. Glycogen, which is also derived from sugar, is a highly important source of energy for the body.

Exercise, of course, brings on a more rapid oxidation, which is always followed by hunger. Especially is this noticeable in children. The normal temperature of the body is  $37^{\circ}\text{C}$ . ( $98.6^{\circ}\text{F}$ .), and the automatic control of the oxidation which keeps this temperature constant is one of the most marvelous functions of the body. If the waste products, i.e., the products of oxidation, are not carried away by the blood, fatigue results, as indicated in Chapter I.

The gas, carbon dioxide, exhaled by the lungs, is a food for plants. The carbon is retained in the tissues of the plant, while the oxygen

is returned to the air. Thus animals and plants work together in keeping the amount of oxygen in the air constant.

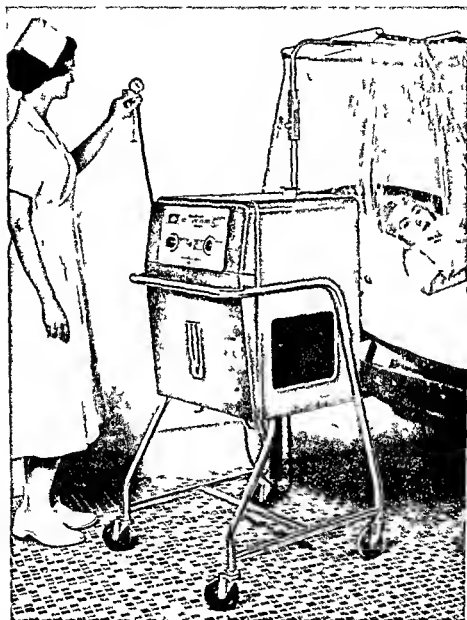


Fig 9—Oxygen Tent. This clear view oxygen tent is used with the hospital central pipeline oxygen system. Note the control at the wall outlet. What are advantages of a central supply system? Courtesy, Ohio Chemical and Surgical Equipment Company.

**OXYGEN IN MEDICINE** Pure oxygen finds an important use in the hospital, especially in the operating room (Fig 8)

There are pathological conditions in which the cells of the body do not receive a normal supply of oxygen from the blood. Such a condition is known as hypoxia (oxygen shortage) and usually may be controlled with an atmosphere of about 50 per cent oxygen. The oxygen for this purpose is stored in steel cylinders and its administration is regulated by observing the rate of flow through a bottle containing water or by a pressure gauge.

A modern method of administering oxygen consists of an oxygen chamber in which the patient is placed in bed, although the oxygen tent is more commonly used in most hospitals. The amount of oxygen to be given is regulated by a motor. In some of our newer hospitals oxygen is piped to beds from a central supply (Fig 9)

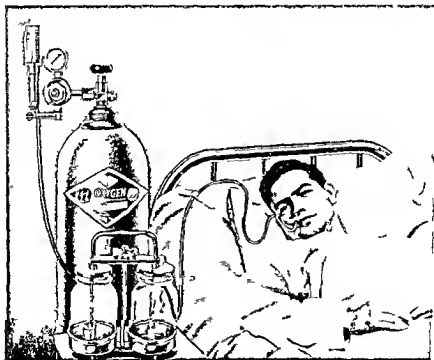


Fig 10—Oxygen Inhalator. The oropharyngeal catheter outfit is of special value for high concentrations of oxygen and as a substitute for an oxygen tent when tent is not available. What is the advantage of the humidifying and dropping jar assembly as shown to the patient's right? Courtesy The Ohio Chemical & Mfg. Co.



Fig 11—Nasal Mask. The nasal mask is suitable for high concentrations of oxygen or oxygen helium therapy. Why is this type of mask convenient in the hospital, and much preferred on commercial air lines? Courtesy, The Ohio Chemical & Mfg Co

A much more economical method of producing a high concentration of oxygen in the blood is by means of the nasal catheter (tube), the insertion of which in one nostril with oxygen flowing briskly (two liters per minute) will supply an inspired air containing 30 to 35 per cent of oxygen, while the use of two catheters furnishes about 40 per cent oxygen (Fig. 10). A convenient type of nasal mask is shown in Fig. 11.

The objections to the uncomfortable use of a nasal catheter, and the initial expense of the other methods mentioned, have resulted in still another method of administering oxygen (Fig. 12).

In cases of accidental interference with respiration, such as occurs in *asphyxia* (condition of lifelessness) and drowning, where normal respiration is either interfered with or cut off for short periods, oxygen is administered in a concentrated form by means of an inhalator. With this apparatus (Fig. 13) regulated amounts of oxygen are released through a rubber mouthpiece into the



Fig 12—An Open Top Oxygen Tent The air is kept cool by a small ice container back of the patient's head. An oxygen flow of four liters per minute maintains a concentration of about 50 per cent around the patient's face. What are the advantages that can be claimed for this type of tent? Courtesy, Warren E Collins Inc

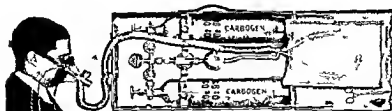


Fig 13—Oxygen Inhalator The oxygen inhalator is used in cases of asphyxia as in drowning and exposure to poisonous gases. Artificial respiration is applied with the administration of oxygen. What municipal department should be equipped with inhalators?

patient's mouth, thus bringing the oxygen content of the blood up to normal.

In certain types of surgery, such as dentistry, nitrous oxide (laughing gas) is used as an anesthetic. Oxygen is mixed with the nitrous oxide to avoid asphyxiation. Any inflammation in the lungs caused by an abnormal condition (reduced pressure) of the air will interfere with the normal supply of oxygen to the blood, and healthy



Fig 14—A Face Tent This newer device is designed for maximum patient comfort. What are some of its advantages compared to the conventional oxygen tent? Courtesy, Ohio Chemical and Surgical Equipment Company

persons will begin to show symptoms of oxygen hunger. This is especially true with aviators, miners, and deep-sea divers. Such persons must frequently resort to the use of pure oxygen. This is supplied from cylinders in carefully regulated amounts, through the breathing helmets. The lightness (92 per cent of the lifting power of hydrogen) and rapid diffusibility of helium gas has made possible an oxygen-helium agent for use with anesthetics in the treatment of asthma, pneumonia, and other respiratory diseases. The helium eases the burden on weakened lungs. It is used as a synthetic air (80 per cent He, 20 per cent  $O_2$ ) for deep-sea divers and under-



Fig 15—Helium Oxygen Therapy Helium because of its low specific gravity as compared to air (0.138 to 1) and its consequently high diffusibility recently has found a use for the relief of various types of respiratory obstruction How will the addition of helium to gaseous anesthetics affect the muscular effort of breathing? Courtesy Ohio Chemical and Mfg Co

water tunnel workers to decrease the danger from caisson disease or the 'bends,' a painful condition caused by sudden expansion of nitrogen from the air dissolved in the blood This use of helium to replace nitrogen depends upon the fact that helium is about 40 per cent less soluble in the blood than is nitrogen (Fig 15)

Oxygen finds another important use in the hospital in ascertaining a patient's *basal metabolic rate* The basal metabolism is the smallest amount of energy required to maintain life when all activity is reduced to a minimum In practice this is measured by determining the amount of oxygen consumed in a given period by the patient when at rest The basal metabolic rate, then, indi



cates the lowest amount of energy required for the body to maintain normal metabolism. Any metabolic rate above normal is indicated by + and below by -. Since there is a normal rate of metabolism in good health, any deviation one way or the other, if excessive, may be an indication of either a present or a future trouble.

### Oxygen Requirement:

The place and value of oxygen with respect to maintaining life deserve some discussion. Even when the body is perfectly quiet and there is no food to be oxidized, the average person requires some 15 to 18 ml. of oxygen per inspiration. If we consider that approximately one-fifth of the air is oxygen, and that one-fifth of the oxygen in the lungs is absorbed by the blood from the lungs, the amount of air inhaled at every inspiration must be about 25 times 15 or 18 ml., or about 400 ml. per inspiration. The amount of the air intake of course will be greatly increased when food is ingested and the person is actively engaged in some form of exercise. To meet any sudden demand of the tissues for oxygen, alteration in lung ventilation must take place, since the body is not capable



Fig 16—A Resuscitator This instrument provides gentle positive and negative pressures to restore natural breathing Why is the position of the head of the patient of importance? Courtesy, Ohio Chemical and Surgical Equipment Company

of storing a reserve supply of oxygen as it ordinarily may do in the case of foods.

If for some reason as in drowning, gas poisoning, and other forms of suffocation, the respiratory mechanism of the body becomes incapable of supplying the tissues with the necessary amount of oxygen, destructive action begins in the cells and prompt measures of resuscitation must be used. This lack of oxygen in the body, hypoxia, is generally relieved by prompt oxygen therapy (Fig 13). However if the condition has been gradual and over an extended period, as in circulatory disturbances of cardiac origin in anemic conditions or in inflammatory conditions of the lungs where there has been fever associated with disease and also where the demand for oxygen in the tissues has been greatly increased—then the cells of the nervous system in particular, the heart and other organs of the body will have been damaged to such an extent that even oxygen therapy may be ineffective. In such cases oxygen therapy may not be considered a specific any more than would be food to one who through starvation has passed beyond the point of assimilation.

It is interesting to know that a candle goes out in air which contains less than 17 per cent of oxygen, but human life will continue, provided other conditions are normal.

From these brief statements it is evident that there are various types of hypoxia, produced by inadequate oxygenation, such as those encountered in pulmonary involvements, circulatory disturbances and in lessened capacity of the blood to carry oxygen.



Fig 17—Effect of Decreasing Pressure of Oxygen. At all altitudes the air contains approximately 21 per cent oxygen. The effect of a decreasing pressure of oxygen on the human body is illustrated in the photographs of a burning candle at barometric pressures corresponding to elevations of 1000 5000 10000 15000 20000 and 25000 feet. Does this correspond to the weakness of the human body and danger of sudden collapse when there is not a normal supply or partial pressure of oxygen in the lungs?

### Symptoms of Hypoxio:

In asphyxia, oxygen deprivation is very rapid, loss of consciousness ensuing with possible convulsions before death. At such times, the most effective treatment is artificial respiration, or the inhalation of oxygen mixed with carbon dioxide, the carbon dioxide being used to stimulate deeper breathing.

On the other hand, slowly developing hypoxia impairs the mind and senses to such an extent that the patient is almost unaware of his condition. The pulse is rapid and feeble, the symptoms being somewhat like the effect of an overdose of alcohol. Headache, excitement, and loss of self-control may follow. The unrecognized failure of judgment on the part of one suffering from slowly developing oxygen shortage is a serious danger because the victim persists in continuing his activities at a time when his condition calls for rest and more oxygen. He does not recognize these delayed symptoms until too late for remedy.

As already mentioned, at sea level approximately one-fifth of the air is oxygen. However, at higher levels, as on mountain tops, the lowered atmospheric pressure diminishes the oxygen per unit volume of air (Fig. 17) to the point where all body functions are



Fig 18—"Air Lock" Helps Babies Breathe. The oxygen-air pressure lock approximates the air pressure, oxygen supply, temperature, and humidity prevailing in the womb just before birth. Air pressure fluctuates automatically, serving to draw out mucus which might choke the infant. *Courtesy, Loewenstern Corp.*



Fig. 19—Portable Oxygen Cylinder. This makes possible oxygen therapy on a first aid basis. The equipment is relatively inexpensive. Where might equipment of this type be made available for emergency use? Courtesy: Inde Division, Union Carbide Corporation.

more or less inhibited. Respiration may even fail temporarily, resulting in fainting or *syncope* or the heart itself may fail to function.

### Guide for Oxygen Therapy

There are many symptoms of oxygen starvation. The nurse, and the anesthetist in particular, must be on the outlook for indications of a lack of oxygen in the patient. A blue colored skin called *cyanosis* (si an-o sis), is a typical symptom of asphyxia. Blue finger tips and cyanosis of the face constitute the most reliable index of hypoxia and the need for immediate oxygen therapy. When cyanosis is evident, the pulse is rapid and the respirations are quick.

ened, but they are more shallow than normal. In combating this condition by increasing the oxygen concentration of the inspired air, it has been observed by different investigators that the higher the concentration of the oxygen the slower will be the pulse. A slow pulse then will indicate that the patient is breathing more deeply and that hypoxia is being relieved. From this it is evident that the pulse can act as one of the best guides in determining the need for oxygen, even before cyanosis is evident.

Within recent years, experiments have shown that the optimum concentration of oxygen for therapy is somewhere between 40 and 60 per cent, and that any concentration below 30 per cent is of scarcely any value. Higher concentrations of oxygen, with the likelihood of not getting enough  $\text{CO}_2$  in the inspired air to stimulate the respiratory centers in the brain, tend to suspend breathing. The nasal catheter method that is commonly used in hospitals supplies up to 35 per cent of oxygen, an amount which, if continued, will provide for the patient's comfort.

A new development in the medical use of oxygen is termed *hyperbaric* (high pressure) *oxygen therapy*. Here the patient, and those immediately attending him, are subjected to elevated oxygen pressures with the result that more than the normal amount of oxygen is carried in the blood stream. Huge pressure chambers are constructed to utilize oxygen in this fashion. At the present time this type of oxygen therapy appears promising, but it is still largely in the experimental stages.

### SELF-TESTING QUESTIONS

18. What is the relation between oxygen and hemoglobin?
19. In what ways is oxygen used in hospital practice?
20. What is the difference between hypoxia and cyanosis?
21. Can hypoxia exist without cyanosis?
22. What has the basal metabolic rate to do with oxygenation in the body?
23. What is oxygen therapy? What is the requirement of oxygen by the body?

### SUGGESTED ACTIVITIES

#### I. THOUGHT PROVOKING QUESTIONS

1. Why is so much of the earth's oxygen found in combination?
2. Why do not oily rags used by mechanics undergo spontaneous combustion?
3. Name three fireproof substances and explain why they are fireproof.
4. Explain the successive use of paper, wood, and coal in producing a coal fire.

- 5 What precautions must be observed to prevent surgical instruments from rusting? To prevent plant and animal food from decaying?
- 6 In extinguishing a fire what principles must be kept in mind?
- 7 What precautions should be observed to prevent spontaneous combustion?
- 8 Does the term "combustion" always involve oxygen? Explain
- 9 Why is oxygen considered the most important element?
- 10 Why is oxygen essential to life?
- 11 Vegetable or drying oils on cloth may undergo self ignition Why do not oils used on dusting cloths and mops start fires?
- 12 In a mine where a candle will burn, a man may get enough oxygen to live How do you account for the fact that a candle will burn on top of Mount Everest, but man cannot live there?
- 13 How do you explain that fanning a fire may in some instances put it out and in other cases makes it burn better?
- 14 What factors determine the rate of oxygenation of the aluminum in a photoflash bulb?
- 15 How do you account for the fact that housewives have been killed by throwing dust collected from floors into an incinerator or furnace?
- 16 In what common disease is there insufficient lung tissue to absorb adequate oxygen from the air?
- 17 How can you identify a gas having no color, odor, or taste?
- 18 How does hypoxia differ from anoxia?

## II VOCABULARY TESTING OF NEW TERMS

electrolysis	hemoglobin	asphyxia
catalytic agent	combustion	inhalator
oxide	enzyme	basal metabolism
oxygenation	spontaneous combustion	oxidase
oxidation	kindling temperature	cyanosis
reduction	hypoxia	syncope

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Fireproof Textiles
- 2 Chemical Fire Extinguishers
- 3 Oxygen Therapy
- 4 Discovery and History of Oxygen
- 5 The Roasting of Iron
- 6 Catalysis in Industry
- 7 Causes and Medical Treatment of Hypoxia
- 8 Devices for the Administering of Oxygen
- 9 High Pressure Oxygen Therapy

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on page 650

# WATER—THE MOST IMPORTANT LIQUID

## CHAPTER OUTLINE

- |   |  |
|---|--|
| <p><b>I OCCURRENCE AND PROPERTIES</b></p> <p>(a) Occurrence</p> <p>(b) Physical properties</p> <p>(c) Chemical properties</p>                           | <p><b>IV HARD WATER</b></p> <p>(a) Objections to use of hard water</p> <p>(b) Water softening</p> <p>(c) Permutit process of water softening</p> <p>(d) Exchange resins</p>  |
| <p><b>II IMPURITIES IN NATURAL WATER</b></p> <p>(a) Mineral water</p> <p>(b) Organic matter</p> <p>(c) Analysis of water</p>                            | <p><b>V PHYSIOLOGICAL IMPORTANCE OF WATER</b></p> <p>(a) A component of protoplasm and tissues</p> <p>(b) A component of all body fluids</p> <p>(c) A tissue lubricant</p> <p>(d) A temperature regulator</p> <p>(e) An aid in digestion</p> |
| <p><b>III PURIFICATION OF WATER</b></p> <p>(a) Distillation</p> <p>(b) Boiling</p> <p>(c) Filtration</p> <p>(d) Aeration</p> <p>(e) Sewage disposal</p> |  |

## I. OCCURRENCE AND PROPERTIES

Just as we are said to be living in an industrial age of metals, so can it be said that we are living in an age of water chemistry, if we think of water in relation to our daily life. In fact, the history of the rise and fall of civilizations and of mankind's economic progress could be written in terms of water—water for navigation, water for irrigation, water for power, and water for drinking and sanitation.

### Occurrence:

Water is the most familiar and abundant of all chemical compounds. Large sections of the colder regions of the earth are covered with it in the form of ice; in the liquid state, it covers about five-sevenths of the earth's surface. The soil contains water which is necessary for the growth of plants, and water vapor is an essential constituent of the atmosphere. Water constitutes more than half the weight of all living organisms and about two-thirds the weight of the human body. Of the amount of water in the human body *one-half is in the muscles, one-fifth in the skin, and one-fourteenth in the blood.* Practically all foods contain high percentages of water as shown in the following table.

Tomatoes	94.3 per cent	Bread	35.3 per cent
Milk	87.0 " "	Beans, dried	12.6 " "
Apples	84.6 " "	Rice	12.3 " "
Potatoes	78.3 " "	Flour	11.9 " "
Beef	73.8 " "	Butter	11.0 " "
Eggs	73.7 " "	Oatmeal	7.3 " "

### Physical Properties:

Pure water is a colorless, odorless, tasteless liquid. In large quantities it may show a bluish or greenish tinge, caused by the reflection and refraction of the light rays and the organic matter suspended in it. It freezes at  $0^{\circ}\text{C}$  \* and boils at  $100^{\circ}\text{C}$ . When water is cooled it contracts until it reaches a temperature of  $4^{\circ}\text{C}$  where it has its greatest density. At this temperature one milliliter (ml) of water weighs one gram. The density of water at  $4^{\circ}\text{C}$  is used as the basis for computing the *specific gravities* (sp. gr.) of liquids and solids. *Specific gravity* is the ratio of the weight of one milliliter of the substance to the weight of one milliliter of water. The specific gravity of mercury is 13.6, which means that one milliliter of mercury is 13.6 times as heavy as one milliliter of water. For expressing the specific gravity of a gas, either hydrogen or air is used as a standard.

When water is cooled from  $4^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ , its freezing point, a slight expansion occurs. In freezing, water expands by about one tenth of its volume. This explains why water, in freezing, bursts water pipes and why ice floats on water.

Water requires more heat than any other liquid or solid to raise a unit mass of it (one gram) through a unit change in temperature ( $1^{\circ}\text{C}$ ). This heat is called *specific heat* and means that water has a specific heat of one calorie per gram per degree C. It has a great heat capacity, and undergoes temperature change more slowly than any other substance. This explains its use in the hot water bottle.

Water also has a high *heat of vaporization*, it requires 539 calories of heat to change a gram of water at  $100^{\circ}\text{C}$  to vapor. These two factors, specific heat and heat of vaporization, explain how the human body maintains its constant temperature. In the change of the vapor back to liquid water, 539 calories of heat will be given off. This is called the *heat of condensation*. It is the high value of heat of condensation that makes steam useful for heating buildings, and it further explains why live steam causes more serious burns than hot water.

When one gram of ice at  $0^{\circ}\text{C}$  changes to water at the same temperature, about 80 calories of heat are absorbed. This heat is known as the *heat of fusion*. This is why ice packs are used to lower body temperature. Each gram of ice in such a pack absorbs 80 calories of heat from the body in melting. In order to change a

\* A comparison of the Cent. grade (C) and the Fahrenheit (F) scales occurs on page 626



gram of water at  $0^{\circ}\text{C}$ . to ice at that temperature, 80 calories of heat must be extracted from the water. this heat is known as the *heat of solidification* of water. It is this operation which is carried on in ice-making plants.

Following are some important physical constants for water:

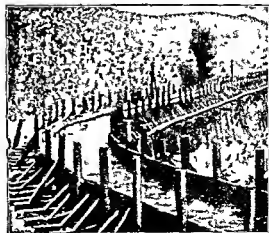
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Freezing point	$0^{\circ}\text{C}$ .
Boiling point	$100^{\circ}\text{C}$ .
Specific gravity	1
Density .	1 Gm. per ml
Specific heat	1 cal per Gm per degree C
Heat of fusion	80 cal per Gm
Heat of vaporization	539 cal per Gm
Heat of condensation	539 cal per Gm
Heat of solidification	80 cal per Gm

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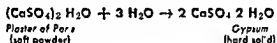
Water is remarkable for its ability to dissolve other substances, and it is the most universal *solvent* known. In fact, even substances like rocks are soluble to a slight extent. Pure water is used in laboratories in making up solutions because most substances dissolve readily in water and chemical action takes place more rapidly in solution. For example, the ingredients in baking powder begin to react as soon as the powder is dissolved. From a biological standpoint the solvent properties of water are of great importance to living organisms as through this medium nutrients are carried to the cells, and waste products away from them.

Fig 1—Water, the Universal Solvent. In the dry regions water is conveyed by flumes to fields so that animal foods may be made available to the plant. What classes of foods are made available to the body by solutions? Courtesy, Eastman Teaching Films, Inc.



## Chemical Properties

Water enters into direct combination with a number of elements and many compounds to form crystalline substances called *hydrates*. A hydrate of special interest to nurses is calcium sulfate or gypsum, the partially dehydrated form being called "plaster of Paris." The latter hydrate when mixed with water "sets" into a hard mass, and finds extensive use in making surgical casts. At such times a coarse mesh bandage (crinoline) is covered with the plaster of Paris powder. The bandage is applied and is then moistened with water, or it is dipped in water, wrung out, and then quickly applied. Since the paste expands slightly upon setting it is necessary to watch the circulation of the part of the body enclosed. The reaction is shown in the following equation:



Notice that the setting of plaster of Paris is a *chemical* change wherein one hydrate is converted into another.

When a hydrate like alum is heated in a test tube, drops of water condense in the cooler part of the tube, leaving a white powder called "burnt alum." The water which assists in the formation of crystals, is called *water of crystallization*, or *water of hydration* (Fig. 2). In this connection, it should be remembered that some crystalline substances like sugar and salt contain no water of hydration and are called *anhydrous* compounds. Sometimes the water of hydration is slowly given off when a crystalline hydrate is exposed to the surrounding dry air, and the crystal crumbles to a powder. Crystallized washing soda is such a compound and it is said to be *efflorescent*. On the other hand, a compound such as anhydrous calcium chloride which takes up atmospheric water, is described

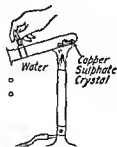
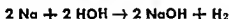


Fig. 2—Water of Crystallization. How can you deter

as *hygroscopic* Substances that are sufficiently hygroscopic to finally pass into solution are said to be *deliquescent*

Although water is a very stable compound that resists decomposition by heat, and is not a very effective oxidizing agent, it does react with many elements Active metals like sodium and calcium displace hydrogen from cold water

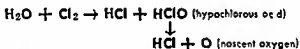


while others like magnesium and iron displace hydrogen only from steam

Certain nonmetals react with water It is the oxidizing action of steam upon glowing coke (carbon)



that furnishes one of the cheapest sources of hydrogen, this mixture of gases, carbon monoxide and hydrogen, is an important fuel called *water gas* A few active nonmetallic elements like chlorine, instead of liberating hydrogen as some metals do, react with the hydrogen in water to liberate oxygen



Water unites with some oxides (called *anhydrides*) to form bases and with others to form acids Thus with some oxides of metals it forms bases (lime changed to calcium hydroxide), while with some oxides of nonmetals it forms acids (carbon dioxide with water changed to carbonic acid, i.e., soda water) Reactions of water with many compounds, such as foods, to break them down into simpler substances, a process called *hydrolysis*, are discussed later in the book

Under the discussion of oxidation you learned that iron rusts in the presence of moisture It has been found also that other chemical reactions will not take place unless a trace of moisture is present For instance dry hydrogen gas, sulfur, phosphorus, and carbon will not burn in perfectly dry oxygen This evidence proves that water is a very important catalyst probably the most important of all

#### SELF-TESTING QUESTIONS

- 1 Name four results of the absence of water in the human body
- 2 State the occurrence of water
- 3 What are the chief physical properties of water?
- 4 What is specific gravity? Specific heat? Heat of vaporization?

5. Why is the temperature of the body constant?
6. What is a hydrate?
7. What is water of crystallization?
8. Why is plaster of Paris used in making surgical casts?
9. What two large classes of compounds are formed when water unites with anhydrides?
10. How do some nonmetallic elements differ from active metals in the presence of water?

## II. IMPURITIES IN NATURAL WATER

Since water is an excellent solvent, naturally occurring water contains more or less matter derived from the soil with which it has come in contact and through which it has percolated. Sea water, for instance, contains about 3 per cent of ordinary salt. Even rain water contains dirt, and gases such as  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$ , dissolved from the air. This foreign matter in water is either *mineral* or *organic* matter, and may be either dissolved or suspended in the water.

### Mineral Matter:

Common salt and various compounds of calcium, magnesium, and iron constitute the usual mineral content found in *natural water*. If the quantity is abundant the water is difficult to lather with soap and is called *hard water*, while water which contains little or no mineral matter lathers easily and is called *soft water*.

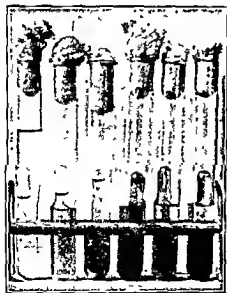


Fig 3—Testing Water for Sewage Contamination. *Bacillus coli* in water is an indication of sewage contamination, since it is an organism whose habitat is the colon of man. This organism decomposes milk sugar with the formation of acid and gas. The three tubes on the left show this gas formation, the inverted inner tube acting as a gas trap. What common diseases are often traceable to water contamination? Courtesy, E Buchanan, Cleveland, Division of Health.

## Organic Matter:

Products derived from the decomposition of plants and animals, and possibly from sewage, comprise the organic matter which is partially suspended and partially dissolved in the water. This organic matter serves as food for bacteria, many of which cause disease. Water from shallow wells and rivers in thickly populated districts is quite apt to be highly contaminated with pathogenic germs. Typhoid fever, dysentery, and cholera are often contracted by drinking water which has been polluted by bacteria carried by those afflicted with the disease. Sickness, directly traceable to water, frequently is due to these disease bearing organisms.

## Analysis of Water:

By evaporating a definite amount of water to dryness and weighing the residue, the total amount of solid matter in the water can be determined. An examination of the composition of the residue is called *mineral analysis*.

## ANALYSIS (PARTS PER MILLION) OF PUBLIC WATER SUPPLIES

City	Solids	Metals				Radicals				Hardness (as CaCO <sub>3</sub> )
		Calcium	Magnesium	Iron	Sodium Potassium	Bicarbonate	Sulfate	Chloride	Nitrate	
New York, N. Y.	28	4.5	1.2	0.04	1.1	11	7.7	1.0	0.49	16
Philadelphia, Pa.	70	12.0	3.3	0.07	5.4	46	12.0	2.9	1.10	44
Detroit, Mich.	99	27.0	7.0	0.20	2.0	102	7.4	4.5	0.08	96
Cleveland, Ohio	159	35.0	8.4	0.07	5.6	13	25.0	11.0		122
Chicago, Ill.	183	36.0	10.0	0.40	Na 4.6	144	10.0	6.0	1.80	131
St. Louis, Mo.	187	26.0	5.1	0.11	26.2	40	73.0	10.0	11.00	86
Los Angeles, Cal.	279	39.0	16.0	0.0	34.0	165	59.0	28.0	Trace	163
San Francisco, Cal.	369	38.0	18.0	.	70.0	276	36.0	76.0		166
Tampa, Fla.	1273	113.0	33.0	0.48	275.0	176	92.0	548.0	2.80	418

An analysis of this kind is of great importance in determining whether the water in question would be adaptable for manufacturing purposes, such as for use in steam boilers and in laundries. An examination to determine the amount of organic matter, the composition of the products (mostly ammonia, nitrites, and nitrates),

and the number and kind of bacteria living upon the organic matter is called *sanitary analysis*. Making such an analysis is necessary for the health of any community. It is not sufficient merely to make a *bacteriological analysis*. In this connection, it is important to remember that the appearance of water is not a criterion of its purity, for clear, sparkling water is often contaminated with dangerous germs. Only a trained chemist and bacteriologist should be employed to make a trustworthy analysis of water.

### SELF-TESTING QUESTIONS

- 11 What constitutes mineral matter in water?
- 12 When is water soft?
- 13 What comprises the organic material in water?
- 14 What diseases may be caused by contaminated water?
- 15 What is a mineral analysis? A sanitary analysis?

### III. PURIFICATION OF WATER

Because all natural waters contain bacteria, some of which are disease causing (pathogenic bacteria), and because water contaminated with sewage is potentially very dangerous to health, different methods of purification have been worked out. By some methods the harmful impurities, mostly pathogenic bacteria, are removed, while by others these harmful impurities are only partially removed and the remainder are destroyed.

#### Distillation

Boiling water and condensing the steam, called *distillation*, is the most effective but not the cheapest method of purifying water (Fig. 4). The mineral matter and most of the organic matter are left in the vessel in which the water was boiled. The *distilled* water, as it is called, is used in the manufacture of ice, to some extent for drinking purposes, and by chemists in making solutions.



Fig. 4—Purifying Water. Distillation does not apply merely to water. Why is distilled water used in the laboratory?

## Boiling:

Water may be made fit for drinking purposes by *boiling*, a process which does not remove any dissolved solid material, as the minerals, but does kill the microorganisms which cause disease. This is the simplest method of purifying water for hygienic purposes. For the household supply the water should be boiled about fifteen minutes. During the boiling of the water the dissolved air is expelled. This causes the water to taste flat, but the flat taste may be overcome by aeration, as in the pouring of water from one vessel to another.

## Filtration:

The suspended matter in water, such as clay and undissolved organic matter, may be removed by *filtration*, a very economical method of purifying water. On a small scale this can be accomplished by passing the water through some porous clay, such as the Pasteur filter which consists of an unglazed porcelain cylinder



Fig. 5—A Slow Sand Filter. What is an objection to this method of filtration?

surrounded by a metal case. In this way bacteria and suspended matter are filtered from the water as it passes through the porcelain to the inside of the cylinder. Substances in true solution, however, cannot be removed by filtration. Such filters are not very satisfactory, as they are not easily kept in working order.

On a large scale, in cities where the water supply comes from *muddy rivers or a polluted lake*, the water is allowed to pass slowly through beds of sand and gravel (Fig. 5), a purely mechanical process. The suspended matter is caught by the sand, but the dissolved impurities still remain in the water. Since not all of the bacteria are on the suspended organic matter, this water is not wholly suitable for household uses.

In the more rapid sand filtration plants, involving both a mechanical and a chemical process, the water before filtration is run into large tanks. Here it is made slightly alkaline, then thoroughly mixed with either aluminum sulfate, iron sulfate, or sodium alumi-

nate to produce a flocculent solid in the water. This insoluble solid settles, carrying with it a part of the suspended particles (Fig 6). The partially purified water is then run through the rapid sand filters, which remove most of the remaining organic matter (Fig. 7). As filtration does not always remove all the bacteria, it has become



Fig 6—Coagulation (A) Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , precipitates finely divided particles of calcium and magnesium compounds which do not readily settle and are difficult to filter. (B) A more flocculent precipitation caused by such precipitants or coagulants as sodium aluminate,  $\text{NaAlO}_2$ , and aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ . How does the size of the precipitated compounds affect clarification? Courtesy, National Aluminate Corp

Fig 7—Rapid Sand Filter. Section of a filter bed composed of about five feet of sand and gravel. What material is not removed by a sand filter?



the practice to treat the water with chlorine, a substance which kills the remaining micro-organisms. In some plants ammonia gas is fed into the water previous to the treatment with chlorine. The ammonia gas unites with the chlorine to form chloramines which



are in themselves strong bactericidal agents and have the advantage of prolonging the effect of the disinfection throughout the dis



Chloramine



Fig. 8—Before and After Treatment with Alum. A visual reproduction of water purified on. The white dots in each plate are colonies of bacteria. The upper left is from unheated raw water. The upper right is of this water after alum has been added. The lower left is the same water after filtration. The lower right with the fewest indications of bacteria colonies is again the same water after sedimentation, filtration, and chlorination. Does filtration remove all bacteria? Courtesy E. Buchanan, Cleveland Division of Health.

tributional system. In addition the chloramines dispel chlorinous tastes and disagreeable odors. In a few cities activated carbon, a finely divided and specially treated carbon having the ability to condense and hold certain gases, is also used to remove tastes and odors due to algae growths.

### Aeration:

When exposed to the air, water, in time, purifies itself. The oxygen of the air dissolves in the water, acts chemically on the bacteria, and destroys them. The oxygen also oxidizes the suspended organic matter into soluble products, thus depriving the bacteria of food. This process, however, should not be relied upon to render water fit for drinking purposes, because the contaminated water may not have had sufficient exposure to the oxygen of the air to kill all the bacteria. Some cities spray their drinking water into the air, others agitate it by bubbling air through the water or by allowing the water to flow over a series of tile cascades in order to cause a better oxidation of the organic matter and any other substances which ordinarily might impart an unpleasant taste and odor. This method of purification is called *aeration* (Fig. 9).

### Sewage Disposal:

Because of the importance of having water free from disease germs, the problem of supplying the community with safe water is closely related to the problem of sewage disposal. If sewage is allowed to be emptied without treatment into the community source, the organic matter with its feeding bacteria soon renders these bodies of water unfit for drinking purposes as well as unfit for bathing or fishing. Unless this sewage is satisfactorily disposed of, it becomes a menace to the health of the people in the community.

There are several ways by which sewage, that is, human excreta and the waste waters of home, public buildings, and factories, may



Fig. 9—Purifying Water by Aeration. When water is sprayed into the air what other factor besides oxygen enters into the killing of bacteria? What pathogenic bacteria are most likely to be killed?

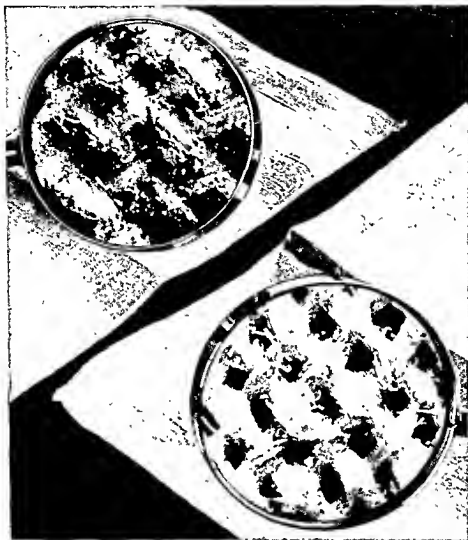


Fig. 10—Contrast between fabrics washed in hard and in soft water. Upper view shows scum from hard water enmeshed in the fibers. How would surgical instruments be affected by washing them in hard water? Courtesy, The Permutit Co., N. Y.

be treated; the problem is to decompose the organic matter upon which the bacteria live, and kill pathogenic bacteria. In some disposal plants the diluted sewage is sprayed into the air in order to oxygenize the organic matter, and reduce the number of bacteria; in other plants the solid wastes are separated from the liquid by screening, sedimentation, and coagulation. This is followed by

bacterial digestion in septic tanks prior to oxygenation, and subsequent chlorination. In the septic tanks (Imhoff) the organic matter is decomposed by the bacteria, which in turn are destroyed by one-celled animals called protozoa. By this treatment what was sewage becomes clear sterile water. The separated solid matter is incinerated, or used as a fertilizer.

### SELF-TESTING QUESTIONS

- 16 Of what does purification of water consist?
17. What is distillation?
- 18 Why does boiling purify water?
- 19 Why does boiled water taste flat and how is this remedied?
20. How may water be filtered in the home?
21. Describe the slow sand filter
22. Explain the rapid sand filtration method of purifying water
- 23 What does aeration do to the water?
- 24 What is the preparatory process in the disposal of sewage and the return of waste waters to rivers and lakes?
- 25 What is the last precaution used on sewage discharge?

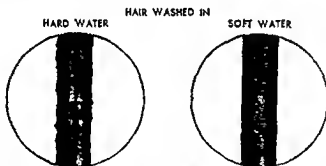


Fig 11—Photomicrographs indicating how water hardness affects hair. How may the resulting gummy residue be removed? Courtesy, Permufit Co., N Y.

## IV. HARD WATER

### Objections to Use of Hard Water:

(1) It is the presence of certain mineral compounds in water which makes the water "hard." When soap is used in this water these minerals react chemically with the soap to form insoluble soaps that have no cleansing properties. They adhere to washed materials and cause them to become harsh and rough to touch, yellowish or gray in appearance, and to develop an unpleasant rancid odor when stored away (Fig. 10). This harshness is a very

undesirable condition especially if the cloth is to be in contact with tender or irritated skin. If iron salts are present, the materials may be discolored, a very objectionable feature in the laundering of clothes. In washing the hair in hard water the sticky, gummy feeling of the hair upon drying is due to these insoluble soaps (Fig. 11). In a somewhat similar way the pores of the skin become partially clogged from washing in hard water (Fig. 12) and in some cases this may produce skin irritations.

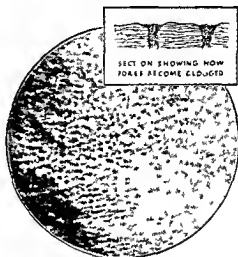


Fig 12—The Skin Washed in Hard Water This is an enlarged photograph of the skin of a girl's cheek. Observe the tiny pores which this magnification makes visible. Note the insertion. Clogged pores may cause what? Courtesy, Permutit Co., N. Y.

(2) In cooking with hard water, the lime salts form on the foods and harden them. Thus when peas and beans are cooked in hard water they do not soften sufficiently because the minerals in the water harden the legumin. In the making of broth and tea these mineral salts interfere with the process of extraction. Therefore, to produce the same strength of tea almost twice the amount must be used with hard water as compared with soft water.

(3) When hard water is heated in boilers, certain mineral salts present become less soluble and deposit layers of hard scale on the sides of the boiler pipes (Fig. 13). Since this scale is a nonconductor of heat, it causes a great waste of fuel. The deposit in a teakettle consists of such lime salts.

### Water Softening:

Since there are many serious objections to the use of hard water several methods have been devised for the removal of the calcium

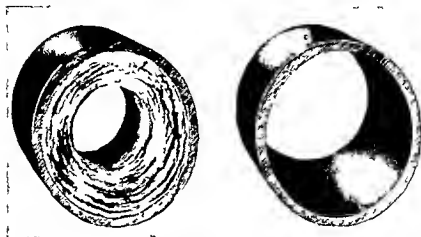
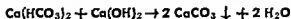


Fig 13—Boiler Scale Notice how the accumulation of the cement like scale cuts down the effective size of the pipe How does scale affect fuel consumption? Courtesy, The Permutit Co, N Y

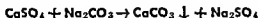
and magnesium salts which cause the hardness There are two kinds of hard water. one, containing the bicarbonates of calcium and magnesium, is called *temporary* hard water; while the other, containing the sulfates or chlorides of these metals, is called *permanent* hard water. Temporary hard water gets its name from the fact that it may be softened by boiling, since heat changes the soluble bicarbonates into the insoluble carbonates of calcium and magnesium.



In actual practice it is more economical to precipitate these salts by the addition of a definite quantity of slaked lime



Permanent hard waters are softened by adding crude sodium carbonate:



On a small scale in the home, washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ ), borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ ), and trisodium phosphate ( $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ ) are frequently used to soften water. In the reactions of all of the foregoing mentioned chemicals, the softening process de-

depends upon the change of soluble calcium and magnesium compounds into insoluble ones which are no longer able to act with the soap to prevent its lathering

Hardness of water, calculated as calcium carbonate, is measured in parts or "degrees" per gallon. One degree is considered as 1 grain per gallon, and is equivalent to 0.017 Gm per liter, or 17 grain parts per million parts, or 17 ppm \* Each 1000 grains of hardness unites with and destroys about  $1\frac{1}{2}$  lbs of soap. One thousand gallons of 10 grain water will destroy 15 lbs of soap which at 30 cents per lb would cost \$4.50

#### DETAILS OF DESIGN

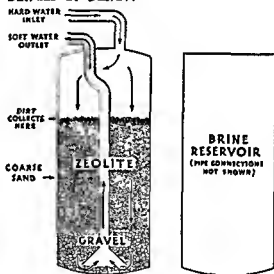


Fig 14—Zeolite Water Softener  
Water is filtered as it is softened.  
Notice where the dirt collects.  
What expense is connected with  
the operation of this system?

#### Permutit Process of Water Softening:

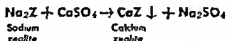
The water softening methods used in homes, laundries, hospitals, and small industrial plants have not been altogether satisfactory since they require close attention for their successful operation. Within recent years this difficulty has been mostly overcome by the *permutit* process of softening hard water. This makes available for the home a water softener that is serviceable, effective, cheap, and easy to operate (Fig 14). The chemical used in this process is natural sodium aluminum silicate, called zeolite, or the manufactured compound called Permutit,  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ , which for brevity

\* To change grains per gallon into ppm multiply by 17 and to change ppm into grains per gallon multiply by 0.0583

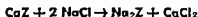


Fig 15—Effect of Hard and Soft Water on Soap The same amount of soap was added to these two containers. Notice how the hard water in the glass to the left destroys soap, and how the soft water in the glass to the right makes a copious lather. What other compounds besides soap soften water? Courtesy, The Permutit Co., N. Y.

may be represented as  $\text{Na}_2\text{Z}$ . When hard water filters through this material the undesirable calcium and magnesium ions are retained as calcium and magnesium zeolites, and the water is then "soft":



After the Permutit has exchanged all its available sodium for calcium or magnesium, it may be automatically regenerated by allowing sodium chloride solution to filter through it.



The soluble calcium and magnesium chlorides are emptied into the drain and the Permutit is again ready for use. By this method it is evident that the only expense is the original cost of the softening unit and the sodium chloride needed for regenerating the zeolite.



Many of our hospitals and homes use this method of water softening

It is to be noticed that the Permutit process is an ion exchange method of softening water inasmuch as the ions which cause hardness are replaced with sodium ions from the zeolite. Hence when water which has considerable hardness is softened in this way, the resulting concentration of sodium ion may make the water unsuitable for individuals on a low sodium diet.

In addition to the previously mentioned methods for softening water there has been introduced a chemical called sodium hexametaphosphate ( $\text{NaPO}_3$ )<sub>6</sub>. This compound softens water by forming soluble complex ions with the calcium and magnesium ions present in the water. In this way the ions responsible for the hardness are effectively removed without the formation of any precipitates. Sodium hexametaphosphate is widely used in commercial and household water softeners. This type of softener is especially useful in cleaning laboratory glassware because it prevents film formation.

### Exchange Resins

The use of ion-exchange resins for water purification is more versatile than the Permutit method because not only calcium and magnesium ions, but also other ions, both positive and negative, can be removed.

The exchange resins are synthetic organic substances, in some respects similar to plastics. They can be designed to perform rather specific functions such as removing all positive ions or all negative ions from natural water or solutions by the process of ion exchange. Use of combinations of resins makes possible a fairly complete deionization to give water which is as pure as distilled water. The ion exchange resins are also finding use for the removal of objectionable ions in the preparation and purification of drugs, vitamins, etc. *Like the zeolite of the Permutit process, these resins can be regenerated after use.*

### SELF-TESTING QUESTIONS

- 26 What are three main objections to the use of hard water?
- 27 What is temporary hard water and how may it be softened?
- 28 What is permanent hard water and how may it be softened?
- 29 Explain the Permutit process of softening water.
- 30 How does the use of the ion-exchange resins differ from the Permutit process?

## V. PHYSIOLOGICAL IMPORTANCE OF WATER

The importance of drinking sufficient water so that there will be plenty for physiological purposes is clearly shown by reading the following paragraphs

### A Component of Protoplasm and Tissues:

We frequently think of foods as including only carbohydrates, fats, and proteins—the energy yielding materials, the substances needed for growth and repair of tissues. We may fail to realize that water too should be considered for the same reasons as foods. Water is as important as the foods we eat.

Approximately two thirds of the body is composed of water. This includes the fluids in the active organs such as the liver, muscles and brain, and in the cells which contain a semifluid called *protoplasm*. If these cells are to be normal and are to carry out chemical changes, they must not be allowed to become too dry. Under normal conditions the amount of water consumed daily amounts to about three or four liters, a large part of which is taken into the body with foods. Water is the medium in which many of the chemical changes in the body take place.

### A Component of All Body Fluids:

The *blood* is the circulating medium of the body for transporting nutrients, waste products, internal secretions (hormones), heat, and the phagocytes which fight invading pathogenic organisms. Normally, the percentage of water in the blood is constant, and if insufficient water is supplied to the blood, the fluid is withdrawn from the tissues. As a consequence the cells suffer (dehydrate) at the expense of keeping the fluid of the blood constant.

*Urine* is the principal medium for the elimination of soluble waste products from the body. Whenever there is not enough water to dissolve and dilute the waste products, and allow them to filter through the kidneys, these organs cease to function properly and become damaged in attempting to eliminate highly concentrated waste solutions.

### A Tissue Lubricant

Water keeps moist such surfaces as the mucous membranes of the eyes, nose, and throat, and thus prevents discomfort. It also moistens the joints, and acts as a solvent in the large intestines, thus aiding digestion and elimination.

### **A Temperature Regulator:**

You have learned that water has a greater capacity for heat than any other liquid or any solid. The body loses heat very slowly. It is when the blood reaches the surface of the body that heat is lost. The blood with its high water content quickly equalizes temperatures as it circulates through the body. The regulation of the body temperature is mainly accomplished by the skin. Cold contracts the capillaries and does not allow much blood to reach the surface of the body. Heat, on the other hand, causes dilation of the capillaries and brings blood to the surface to be cooled. Heat also stimulates the sweat glands to produce more secretion and lower the temperature. Water then is necessary for perspiration.

### **An Aid in Digestion:**

Food is first dispersed and then acted upon by digestive fluids secreted by different glands. In both cases water is necessary. Moreover, the greater the amount of water the more rapid will be the chemical action and absorption of the digested foods. Furthermore, water is one of the reacting substances during the actual digestion of foods and in many of the other changes which take place in the cells of the body. (See page 417)

From the previous statements it is evident that water is an important substance for maintaining life, and especially so when nutritive materials must be reduced to a minimum. Life without nourishment may continue for several weeks but without water death results in a few days.

### **SELF-TESTING QUESTIONS**

- 31 Why is water important to the protoplasm of the cell?
- 32 Why is water an important part of the blood?
- 33 How does water affect the function of the kidneys?
- 34 State how water aids chemical activity.
- 35 How does water regulate the temperature of the body?
- 36 Mention three ways in which water aids in the digestion of foods.

### **SUGGESTED ACTIVITIES**

#### **I. THOUGHT PROVOKING QUESTIONS**

- 1 If steam is a colorless invisible vapor what is the material we ordinarily call steam?

- 2 What are three facts that make water especially suitable as the cooling liquid for automobile radiators?
- 3 What distinction is made between a mineral and a sanitary analysis?
- 4 How may a nurse quickly purify water contaminated by pathogenic organisms?
- 5 Name some metals that do not react with water
- 6 How is filtration carried out in your city?
- 7 What is the chief danger of a domestic filter?
- 8 Why is a cooling effect produced when a floor is sprinkled with water?
- 9 What is formed when iron reacts with water?
- 10 What kind of impurities will filtration remove from water?
- 11 If you were camping out and suspected the water to be contaminated with typhoid fever germs how would you render it fit for drinking purposes?
- 12 Name some foods other than those mentioned which contain considerable quantities of water
- 13 Can water from its appearance or taste be judged as safe? Explain
- 14 What are the most desirable properties of water to be used for laundering? For drinking?
- 15 Pressure cookers subjected to superheated steam are made of aluminum and of steel Why is steel not preferred?
- 16 During the hardening process of plaster of Paris used in making a surgical cast why doesn't the patient feel the chillness of the moist application?
- 17 In using an ice bag for therapeutic purposes how much heat will be absorbed if the bag contained 200 grams of ice?
- 18 Temporary hard water contains calcium acid carbonate the calcium of which can be precipitated by household ammonia What calcium salt is precipitated?

## II VOCABULARY TESTING OF NEW TERMS

specific gravity	hygroscopic	distillation
specific heat	deliquescent	aeration
heat of vaporization	anhydrous	temporary hard water
heat of condensation	anhydride	permanent hard water
heat of fusion	mineral matter	zeolite
hydrate	organic matter	Permutit
water of crystallization	mineral analysis	protoplasm
efflorescent	sanitary analysis	

III. TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Water Purification in My Community.
- 2 Value of Soft Water in Reducing Costs and Improving Service
- 3 Methods of Water Softening in the Home
- 4 Progress in Treatment of Sea Water
- 5 Water Shortage in Urban Areas

LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 655, 657

## CHAPTER V

# SOLUTIONS—LIQUIDS OF EVERYDAY USE

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### CHAPTER OUTLINE

- I SOLUTIONS, THEIR NATURE AND PARTS
    - (a) Meaning of the term "solutions"
    - (b) Components of a solution
  - II SOLUBILITY
    - (a) Conditions affecting solubility
      - (1) Nature of the solute and solvent
      - (2) The temperature
      - (3) The pressure
    - (b) Saving time in making solutions
    - (c) Concentration of solutions
    - (d) Ways of expressing exact concentration
  - III THE PROPERTIES OF SOLUTIONS
    - (e) Diffusion
  - (b) Osmosis
  - (c) Physiological saline solutions
  - (d) Necessity of normal osmotic pressure
  - (e) Boiling point and freezing point
  - IV COLLOIDAL DISPERSIONS
    - (a) Suspensions
    - (b) Colloidal dispersions
    - (c) Preparation of colloidal dispersions
    - (d) Classification of colloids
    - (e) Properties of colloidal dispersions
    - (f) Gels
  - V EMULSIONS
- 



Fig 1—"The Big Four" in Solutions. Saline Solution, Ringer's Solution, Water, Dextrose. What general precautions must be taken in making solutions? Courtesy, University Hospital, Cleveland, Ohio

## I SOLUTIONS, THEIR NATURE AND PARTS

### Meaning of the Term "Solutions"

In a typical mixture such as powdered iron and sulfur, it is very easy to distinguish one particle from another, while in a compound, such as iron sulfide, every particle is alike in composition. Intermediate between mixtures and compounds are the solutions. Like mixtures, they may be made variable in composition, while like compounds they are uniform throughout. Everyone is familiar with the phenomenon of solution. Sugar or salt in water is a good example of a solution. If you drop a crystal of potassium permanganate into a tall graduated cylinder containing water you may see the slow dissolving of the crystal with the formation of a clear purple color, which in time diffuses slowly through the water until uniformly distributed throughout the cylinder of water. If the

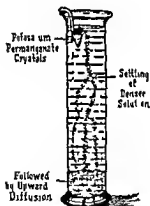


Fig 2—Solution in the Making. The purple black crystals suspended in the paper stirrup just below the water surface slowly go into solution. After the denser solution settles, what force causes diffusion upward?

solution is diluted it is possible to observe that all parts of the mixture appear exactly alike, i.e., it is a clear, *homogeneous mixture*. Evidently there is a tendency for the particles of a substance in solution to distribute themselves uniformly throughout a solvent. Such a process of dispersion is called *diffusion* and applies to gases as well as to liquids. From these statements a *true solution* is to be considered as a *homogeneous molecular or ionic dispersion*.

### Components of a Solution

In making up solutions water is generally used on account of its cheapness, accessibility, and its property of dissolving many substances. A water solution is often called an *aqueous solution*, while

in an *alcoholic solution* the solvent is alcohol. As matter exists in three states *solid*, *liquid*, and *gaseous*, it is possible to form many different kinds of solutions by mixing one form of matter with another. In any solution the substance which is dissolved is called the *solute*, and that substance in which the solute is dissolved is called the *solvent*, for example, in the solution of sugar in water, the sugar is the solute, and the water is the solvent. Water is the best of all solvents. Other common liquids that have great solvent power are alcohol, carbon tetrachloride (Carbena), gasoline (Energene), and ether. It is quite essential that we choose the solvent which is most suitable for the purpose intended. For example, in removing grease spots from clothing we may use gasoline or carbon tetrachloride, if the spot is paint, we use turpentine, but if the spot is sugar, water does nicely.

### SELF-TESTING QUESTIONS

- 1 State three ways in which we are continually dealing with solutions.
- 2 Why is solution of importance to the nurse? To the chemist? To the farmer?
- 3 What is a solution? Define the parts of a solution.

## II. SOLUBILITY

### Conditions Affecting Solubility:

By far the most familiar type of solution is a solid dissolved in a liquid. For such solutions the extent of solubility of the solute depends upon

(1) **THE NATURE OF THE SOLUTE AND SOLVENT** The nature of both the solute and the solvent has a very definite influence upon solution. No material is absolutely *insoluble*. Marble, for instance, will dissolve to a slight extent in water. Some substances which are but slightly soluble in water are readily soluble in certain other solvents. Greases and oils show practically no tendency to dissolve in water, but they are easily soluble in carbon tetrachloride, ether, gasoline, or trichloroethylene.

(2) **THE TEMPERATURE** Generally when we wish to hasten the solubility of a substance we use heat, since the solubility of most substances increases with a rise in temperature. On the other hand, a few substances decrease in solubility with a rise in temperature. This latter condition may be clearly shown by boiling some clear limewater, which becomes turbid as a result of the separation of



some of the calcium hydroxide. The solubility of a solute usually is defined as the weight in grams of any solute that will dissolve in any given amount of solvent (usually 100 grams of water) at the given

### SOLUBILITY

Substance	Weight dissolved by 100 grams of water at		
	0° C	20° C	100° C
Sodium chloride	35.7	36.0	39.8
Potassium nitrate	13.3	31.6	246.0
Calcium hydroxide	0.185	0.165	0.077

*temperature* A study of the above table shows that sodium chloride increases slowly in solubility with a rise in temperature while potassium nitrate (saltpeter) increases greatly. On the other hand note that calcium hydroxide (slaked lime) decreases in solubility. Most solids act like the potassium nitrate in their change of solubility with temperature. The solubility of gases in liquids is in general lowered by a rise in temperature.

(3) **THE PRESSURE** This is another factor to be considered in solubility but mainly as applied to gases, as the solubility of gases increases with an increase in pressure (Henry's law). Thus in making carbonated drinks, the amount of carbon dioxide dissolved will depend upon the pressure as well as the temperature. Variations in pressure do not affect the solubility of solids in liquids.

### Saving Time in Making Solutions

Sometimes it is desirable to hasten the process of solution of a solid, especially if there should be no unnecessary delay, such as in the preparation of a solution for a hypodermic injection. Time will be saved if the following suggestions are kept in mind.

(1) *Powder* the solid finely in order that as much surface as possible may be exposed to the solvent, for a solid dissolves at its surface only. (2) *Stir* or *agitate* the mixture continuously, so that the saturated solution around the solid may be swept away and thereby allow fresh portions of the solvent to come in contact with the solid. (3) *Heat* the liquid if necessary, that is, provided that heat does not cause any change in its chemical properties or introduce the danger of fire.



Fig. 3—To save time in making a solution

powder

stir

heat

### Concentration of Solutions:

When a solution contains a small amount of a dissolved material in proportion to the amount that could be dissolved, it is said to be *dilute*. When it contains a *large* amount it is *concentrated*; and when it contains all it can normally dissolve at a given temperature, it is *saturated*. As was mentioned in a previous paragraph, it is a general rule that the solubility of solids increases with rise in temperature and so at a higher temperature more of the solute will be in solution. Now if a solution saturated at a high temperature is allowed to cool to room temperature we might expect the extra amount of the solute to fall out of solution in the form of crystals as the temperature falls. This is generally the case, but sometimes when a hot solution is cooled slowly and is not disturbed, no solid immediately separates, even though the solution contains more solid than it can ordinarily dissolve at that temperature. This produces what is known as a *supersaturated solution*. Crystallization, however, will appear in time if such a solution is allowed to stand or is shaken, for example, often when jams or jellies are made, crystals of sugar slowly form after the material has cooled proving that the solution was supersaturated. Another familiar example of supersaturation often occurs when boiling down sugar to make thick fudge syrups and sauces. At such times avoid stirring, otherwise crystals of sugar collected on the sides of the pan during evaporation may be scraped off to cause more crystals to form, and thus produce a "grainy" consistency.

### Ways of Expressing Exact Concentrations:

In using the term "concentration," we may be referring to one of several things, so it is well for us to keep in mind the conditions under which we use the term. In medicine, we commonly use the term *percentage* when referring to how much of the solute is in solution. This may refer to weight in weight, weight in volume, or

volume in volume Since one gram of water occupies essentially one milliliter at room temperature, it is permissible, for convenience, to measure water by volume instead of by weight in preparing aqueous solutions.

The use of *per cent* for expressing concentrations of solutions is widespread in hospital and pharmaceutical practice, hence some illustrations will be given A 4 per cent by weight glucose solution means that there are four parts by weight of glucose in one hundred parts by weight of solution One would therefore prepare 100 grams of a 4 per cent by weight glucose solution by dissolving 4 grams of this sugar in 96 grams (or ml) of water

An important solution in hospital procedure is the physiological saline solution which is approximately a 0.9 per cent concentration of sodium chloride in water To prepare 500 grams of this solution the technician would reason as follows

0.9 per cent of 500 grams =  $0.009 \times 500 = 4.5$  grams Therefore use 4.5 grams of salt

500 grams - 4.5 grams = 495.5 grams Hence use 495.5 grams (or ml) of water

The solution is then prepared by dissolving the salt in the water to give 500 grams of solution Percentages calculated in this way are on a weight weight (W/W) basis

When both the solute and the solvent are liquids the volume volume (V/V) per cent is convenient to use because no weighing is necessary The 70 per cent solution of alcohol and water used in the wards is in the proportion of 70 ml of alcohol made up to 100 ml with added water

The chemist often expresses concentrations on a *molar* basis This shows the number of gram formula weights (moles) of solute present in one liter of solution A one molar (1M) concentration of sodium hydroxide NaOH, formula weight of 40 is prepared by dissolving 40 grams of this compound in sufficient water for one liter of solution Often concentrations other than one molar are more useful in practice, and one finds two molar (2M), one tenth molar (0.1M), etc

Chemists also employ *normal* concentrations when referring to the *reactive ability* of an acid, base, or salt solution A one normal solution contains one gram equivalent of the active radical per liter of solution For example, a one normal solution (1N) of any acid contains enough of that acid in a liter of solution to yield 1.008 grams of replaceable hydrogen A one normal solution of a



Fig 4—Measuring the Volume of a Solution The volume of a solution can be measured to one hundredth of a milliter by use of burets pictured here Can you name some other pieces of laboratory equipment used for measuring volumes of solutions? Courtesy Kimble Glass Company

base contains sufficient base per liter of solution to provide 17 008 grams of hydroxyl, while a one normal solution of a salt contains as many grams of the negative radical per liter of solution as will react with 1 008 grams of hydrogen from an acid Thus equal volumes of all solutions of the same normality are exactly equivalent Again, concentrations like 2N, 0 1N, and 0 01N, etc are also used in actual practice

Notice that *molar* refers to the concentration of moles of solute, whereas *normality* deals with the concentration of the active

radicals of acids, bases, and salts. Normal and molar solutions must never be confused, for though in some instances they are the same, in many cases they are quite different. To illustrate, in the case of sodium hydroxide ( $\text{NaOH}$ ) a molar and a normal solution are of the same concentration, but in the case of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) a one molar solution is also a two normal solution. The following table will help to bring out these facts.

Compound	Formula	Grams per Liter in a	
		Molar Solution	Normal Solution
Sodium Chloride	$\text{NaCl}$	56.44	58.44
Sodium Sulfate	$\text{Na}_2\text{SO}_4$	142.04	71.02
Hydrochloric Acid	$\text{HCl}$	36.46	36.46
Orthophosphoric Acid	$\text{H}_3\text{PO}_4$	98.00	32.67
Sodium Hydroxide	$\text{NaOH}$	40.00	40.00
Barium Hydroxide*	$\text{Ba}(\text{OH})_2$	171.35	85.68

A modification of normality for expressing concentrations of very dilute solutions is the *milliequivalent* ( $\text{mEq}$ ) notation. This is particularly useful in clinical procedure for stating concentrations of electrolytes (ions) in body fluids and in parenteral fluids (See page 465). One milliequivalent weight is the one thousandth part of a gram equivalent weight. Thus one milliequivalent of sodium ion is 0.023 grams (23 milligrams). As an illustration, a container might be labeled 150  $\text{mEq}$  of  $\text{Na}^+$  per liter.

### SELF-TESTING QUESTIONS

1. What conditions affect the solubility of a solid in a liquid? The solubility of a gas in a liquid?
2. How may time be saved in making solutions?
3. How do you distinguish between the terms dilute, concentrated, saturated, and supersaturated solutions?
4. What is a molar solution? A normal solution? Of an acid? Of a base? Of a salt?

\*In practice barium hydroxide is not sufficiently soluble in water to make the concentrations given here.

### III. THE PROPERTIES OF SOLUTIONS

#### Diffusion:

As has been explained, the solute distributes itself uniformly throughout a solution. In the case of gases, we learned that the greater the pressure the greater the solubility. We can best understand diffusion by comparing it to this. Evidently there is a pressure set up by a substance as it dissolves. As we know, pressures tend to equalize, and it seems that as a substance dissolves and sets up a pressure at the point of greater concentration, this pressure tends to equalize throughout the solvent by forcing the particles of the solute to all parts of the solution until there is a uniform concentration throughout the solution. This intermingling of two substances resulting from the motion of individual particles is called *diffusion*. Density markedly affects diffusion, and consequently liquids diffuse less readily than gases, while but few solids in contact with each other diffuse.

#### Osmosis:

Certain membranes will selectively permit solvent molecules but not solute molecules to diffuse through them. These membranes are found in plants and animals, and may also be prepared in the laboratory from cellophane, collodion, etc. Since they show a selective action they are described as semipermeable, or differentially permeable.

When two solutions of differing concentration are separated by such a membrane, the solvent molecules may pass freely through the membrane in both directions, but the solute particles are prevented from diffusing through the membrane from one solution to the other. The term *osmosis* is defined as the passage of solvent molecules through a semipermeable membrane from the solution of lesser concentration of solute into the solution of greater concentration of solute. Actually the solvent molecules diffuse through the membrane in both directions, but the rate of flow is greater from the more dilute solution. Thus both solutions tend to come to the same concentration. The force responsible for this flow of solvent, not fully understood by scientists, is termed *osmotic pressure*.

As an example, consider two sugar solutions, one a 2 per cent solution and the other a 5 per cent solution, separated by a suitable semipermeable membrane. A film of collodion may be used

Osmosis will take place, and in a given time more water molecules will pass from the 2 per cent solution into the 5 per cent solution than will pass from the 5 per cent solution into the 2 per cent solution. Since the sugar molecules cannot diffuse through this membrane, the 5 per cent solution becomes progressively diluted by gaining water, and the 2 per cent solution becomes concentrated by losing water. If conditions permit, the two solutions will ultimately attain the same concentration, and are then said to be *isotonic*.

The principle of osmosis is very important in many physiological processes, such as the assimilation of nutrients, formation of urine, maintenance of blood volume and distribution of water. The principle is also applicable in many clinical treatments such as depletion of edema. Other interesting examples of osmosis are the passage of soluble mineral salts from the soil into plant rootlets, the rise of sap in trees, and the swelling of seeds during germination.

### Physiological Saline Solution

In the physiological salt solution the solute, sodium chloride, is present in approximately the same concentration as are the salts in the blood. In other words it is a solution that is approximately isotonic with the blood in regard to salinity. Practice and conditions very much affect the concentration must be, but under normal conditions it is usually between 0.85 per cent and 0.9 per cent sodium chloride.

Ringer's solution, which is used in laboratory work, is supposed to contain the salts of the blood in exactly the same proportions as they occur in the blood.

A physiological salt solution is used under the following conditions

- 1 When the body has lost much fluid, as in hemorrhage
- 2 Postoperative shock
- 3 When a septic condition exists, as in streptococcus infection
- 4 When a patient is dehydrated and unable to take the necessary fluids by mouth

If the solution contains a greater percentage of salt than the blood, the solution is said to be *hypertonic*, while if it contains a lesser concentration it is said to be *hypotonic*. If the concentrations are the same, the term *isotonic* applies.

### Necessity of Normal Osmotic Pressure

If placed in *hypotonic* saline solutions, the red corpuscles will begin to swell and finally rupture because of the water passing in through the cell wall by osmosis to dilute the more concentrated cell contents. This disintegration of the red corpuscles is called *hemolysis*, and the blood is said to be *laked*. Hemolysis taking place after a salt infusion causes death. In a *hypertonic* salt solution, just the reverse process takes place, namely, the liquid flows out from the corpuscles, which then become shrunken or *crenated*, a condition called *plasmolysis* in plant physiology.

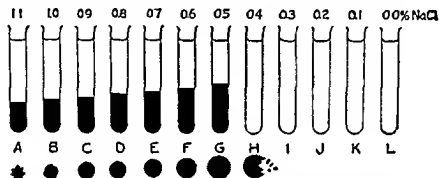


Fig. 5—How hypertonic and hypotonic solutions injure cells. The solutions of NaCl in tubes C and D are about normal or physiological; that is they are isotonic with human blood. In them the red corpuscles retain their normal shape and size. The hypertonic solutions in A and B however make the corpuscles shrink while the hypotonic solutions E, F and beyond make the corpuscles swell. In H in fact the swelling overtaxes the corpuscles and they rupture. Pure water represented in tube L as 0.0 per cent NaCl destroys red corpuscles and most other types of cells.

In case of drugs being administered intravenously, the effects just described must be considered. It oftentimes is necessary to dissolve the drugs in a physiological saline solution. In the cleansing of wounds, a sterile physiological saline solution is used not only on account of its mild antiseptic properties but also for the reason that the tissues are not changed by osmosis. Thus it is evident that solutions used in the body for therapeutic purposes should be isotonic to the blood, and intravenous and subcutaneous medications must be isotonic if red cells are not to be destroyed. However, because of quick oxidation, 10 to 50 per cent solutions of glucose are used intravenously without any apparent damage to the cells.



There are certain pathological conditions when it is advantageous to give a hypertonic solution. For example, in diseases accompanied by edema, frequently a concentrated solution of magnesium sulfate is given by mouth. In this way the high concentration of salt withdraws the fluid from the tissues into the intestine and eliminates it through the intestinal tract.

The food we eat is digested, passes into the blood by osmosis, and then is carried throughout the body. A familiar example of osmosis is the condition which develops when the kidneys become diseased and fail to eliminate salt from their tissues. Too much fluid passes from the blood into these tissues, which then swell, giving rise to edema or dropsy.

### Effect of Solute on the Freezing and Boiling Points of Solvents:

Besides the property of diffusion, there are other physical properties of solutions due to dissolved substances. For instance, the boiling point of a solution of a nonvolatile compound is always higher and the freezing point is lower than that of the pure solvent. The extent to which this takes place depends upon the number of freely moving solute particles present in the solution. Advantage is taken of this latter property in the use of radiator-antifreeze mixtures, such as alcohol and water. The lower freezing point of a solution is indicated by the fact that the salt water of the ocean freezes only near the poles where the temperatures are very low.

Any crystalline substance, as it dissolves, will absorb heat. This is the principle in the use of salt to melt ice and snow, and in the use of ice-salt mixtures to obtain low temperatures.


### SELF-TESTING QUESTIONS

8. What is the significance of osmosis?
9. What is the distinction between diffusion and osmosis?
10. What causes osmosis?
11. What is meant by a semipermeable membrane?
12. What importance is attached to the fact that cell walls are semipermeable?
13. What is a physiological salt solution?
14. How is Ringer's solution made?
15. How do you distinguish between the following terms: Isotonic, hypertonic, hypotonic, plasmolysis, laked, hemolysis?
16. Under what conditions are isotonic salt solutions used?
17. What causes the swelling associated with edema? With an insect bite?
18. What change in physical properties of a solvent is produced by a solute?

## IV. COLLOIDAL DISPERSIONS

In the true solution the particles of the dissolved substance are too small to be seen, and they will never settle out. Evidently the solute is dispersed as individual, fundamental particles, so that the true solution is a *molecular or ionic dispersion*. (In the next chapter it will be learned that in some solutions the dispersed solute particles are electrically charged, and are called ions.)

## COMPARISONS OF TRUE SOLUTIONS, COLLOIDAL DISPERSIONS, AND SUSPENSIONS

<i>Properties</i>	<i>Molecular Dispersions</i>	<i>Colloidal Dispersions</i>	<i>Suspensions</i>
Approximate diameter of particles in millimeters	$\frac{1}{10,000,000}$ mm to $\frac{1}{1,000,000}$ mm	$\frac{1}{1,000,000}$ mm to $\frac{1}{10,000}$ mm	$\frac{1}{10,000}$ to 1 mm
Visibility		With ultra microscope	With microscope or naked eye
Osmotic pressure	High	Low	None
Relative size of molecule of hydrogen and the smallest particle visible under the ultramicroscope, about 3,000,000 magnifications	•		Too large to illustrate here
Diffusibility and filtrability	Passes through membranes and filters	Passes through filters but not through membranes	Does not pass through filters or membranes

## Suspensions:

When particles of very finely divided clay or chalk are dispersed in water one observes a cloudy, milky effect. If the mixture is allowed to stand, the dispersed particles will in time settle out and the liquid portion becomes clear. The milky mixture obtained by

the dispersion of the clay or chalk is referred to as a *suspension*. Muddy water is another *illustration* of a suspension, if the water is permitted to stand the dispersed particles will settle to the bottom of the container. The separation can be accomplished more quickly by filtering.

### Colloidal Dispersions:

Intermediate between true solutions and true suspensions, and merging into each, is a type of dispersion in which the particles are much too large for the true solution and yet too small for the suspension. Such a system, which normally never separates, is called a *colloidal dispersion* or, less correctly, a colloidal solution. The dispersed colloidal particles are either tremendously large molecules, like proteins, or they are aggregates of smaller molecules which can be viewed as clusters. Colloidal particles are in ceaseless, random motion when placed in a dispersing medium, yet it must be emphasized that the colloiddally dispersed material and the dispersing medium are mutually insoluble.

In theory, and usually in practice, all solids and liquids, but not gases, can be treated to produce particles of colloidal size and these particles can then be dispersed in solid, liquid, or gaseous media to give colloidal systems. Since many solids and liquids (metal, acid, base, salt, carbohydrate, fat, protein) can be ground up and dispersed in liquids in which they are insoluble, the study of this branch of chemistry becomes wide in its scope. The table on page 107 shows the eight types of colloidal dispersions.

### Preparation of Colloidal Dispersions.

The formation of colloidal particles may be approached in two different ways, namely, by dispersion methods and condensation methods. An illustration of dispersion methods is the use of colloid mills and homogenizers. These are machines used for breaking down substances by grinding, etc., to give particles of colloidal size. Also, certain insoluble substances are readily dispersed by the action of reagents which bring about disintegration or peptization into particles of colloidal size. Thus, the pepsin of the gastric fluid is effective in disintegrating protein food to give the colloidal peptones. In fact, the disintegration of most foods is brought about through the presence of certain factors (enzymes) in the digestive fluids that disintegrate the food, first into colloidal parti-

## EIGHT TYPES OF COLLOIDAL DISPERSIONS

<i>Dispersed Substance</i>	<i>Dispersion Medium</i>		
	<i>Gas</i>	<i>Liquid</i>	<i>Solid</i>
Gas (as bubbles)		Froths Foams as whipped cream, CO <sub>2</sub> drinks	Solid foams as floating soap, pumice, adsorbed gas
Liquid (as droplets)	Fog as clouds, spray	Emulsions as milk, blood	Jelly, gelatin
Solid (as grains, films)	Smoke as fumes, dust	Gels as glue Cellulose as lacquers cellophane, rayons, plastics	Some alloys, colored glass, precious stones as topaz

cles, and then finally into molecular dispersions, i.e., true solutions. The use of hot water on gelatin provides a further illustration of peptizing a solid to produce a colloid, in this case one which sets to a gel.

Methods of condensation for the preparation of colloids are not as common as those of dispersion. As an example, colloidal gold can be prepared by causing gold ions of a solution to come together and build colloidal clusters of gold atoms. Dispersions of colloidal gold in water have striking colors, the shade of color is dependent upon the size of particle.

## Classification of Colloids:

For practical purposes it is convenient to classify colloidal dispersions which are liquids as *lyophilic* (solvent loving) and *lyophobic* (solvent-hating). Since water is so often the medium in which the colloidal particles are dispersed, the terms *hydrophilic* (water-loving) and *hydrophobic* (water-hating) are in common usage.

In the hydrophilic colloids the dispersed particles have a great attraction for water and consequently this type of colloid is quite stable and generally more viscous than water itself. Examples include starch, glues, gums, gelatin, pectin, and agar, all organic substances. Other hydrophilic colloids appear as semisolids, and in this form are known as jells or *gels*.

Hydrophobic colloids are usually more difficult to prepare and are much less stable than the hydrophilic types. The dispersed particles of the hydrophobic colloid show little or no attraction for water, and for this reason such systems are mobile liquids which have about the same density and fluidity as water. The dispersed particles are usually inorganic in character as evidenced by such examples as colloidal ferric hydroxide, arsenic trisulfide, and gold and other metals. Hydrophobic colloids often appear to be true solutions, and therefore may be referred to as *sol's* as differentiated from solutions; thus, a certain particle size of gold metal dispersed in water produces a gold sol which has the color and general appearance of a dilute potassium permanganate solution.

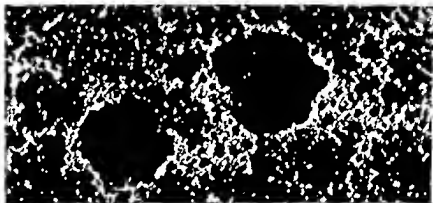


Fig. 6—Electron Microscope. Reflections of movements of colloidal particles by use of an electron microscope which reveals 100 times more detail than is possible with the most powerful light microscope. The picture of these colloidal particles of silica show a magnification of 25 000 diameters; the diameter of an average particle being one millionth of an inch. Courtesy Du Pont Company.

### Properties of Colloidal Dispersions.

(1) **SIZE OF COLLOIDS** In general, the various properties exhibited by colloids stem from particle size. As already noted, the dispersed particles of the colloid are exceedingly small, ranging in diameter roughly from 1 millimicron to 100 millimicrons (see table p. 105). A millimicron is one millionth of a millimeter. Colloidal particles, like solute particles (molecules, ions) of a true solution, pass through filter paper, consequently, to remove colloidal particles, it is necessary to cause them to build up into larger aggregates which can precipitate. This can be accomplished in

various ways. Some colloids owe their permanency to the presence of a protecting agent, itself colloidal, and termed a *protective colloid*. Gelatin is an excellent protective colloid; used in the preparation of ice cream it surrounds the tiny colloidal particles and prevents them from growing and separating. Without the gelatin or some other protective colloid, ice cream would contain rather coarse crystals of ice and of sugar. Milk used for infant feeding may be made more digestible by adding a colloidal protecting agent such as gelatin, gruel, or dextrin to surround the colloidal casein particles and thus prevent the formation of too large curds.

One approach, therefore, in destroying a colloid is to remove or render ineffective any protective colloid present. Later it will be pointed out that colloidal particles are electrically charged. Removing the charge is usually an effective measure for bringing about precipitation.

(2) **DIALYSIS:** It has already been mentioned that colloidal particles, like the solute particles of the true solution, readily pass



Fig. 7—Dialysis. How colloids are separated from crystallids. Refinement and concentration of antitoxin substances by dialysis. Precipitated antitoxic material is placed in parchment membranes and suspended in a current of fresh water. Undesirable soluble salts pass through the membrane by dialysis, leaving the precipitated antitoxic substances within the membrane. In a poisoning case, how could the poison be separated from the stomach contents? Courtesy, Parke Davis & Co.

through filter paper. However, a mixture of colloid and noncolloid (often termed a crystalloid) can be separated by placing the mixture in a parchment bag which is surrounded by water. The colloidal particles are too large to pass through the parchment, which serves as a membrane, but the molecules and ions of any dissolved substance diffuse readily through the semipermeable membrane. As an example, a mixture of starch and salt can be separated by this technique. This method of separation is called *dialysis* (di-al'i-sis). To dialyze, then, means to separate a crystalloid from a colloid by the diffusion of the crystalloid through a suitable membrane. Food, when colloidal, cannot penetrate the intestinal walls and enter the blood. The process of digestion produces crystalloids which are readily absorbed.

In this connection, with the general understanding that crystalloids pass readily through cell walls, while colloids are too large for this action, one must note that in the living organism there are other vital forces at work which may interfere with or modify the expected processes. That there is a difference between living and dead membranes is shown by the fact that sugar in solution will readily pass through a dead or parchment membrane, but will not pass directly from the intestine through the intestinal wall. Without doubt, osmosis plays an important part in the passage of body fluids and their dissolved substances.

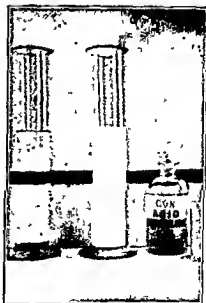


Fig. 8—Colloidal Suspension of Sulfur. Colloidal sulfur is precipitated from a sodium thiosulfate solution by adding a few drops of acid. What determines whether the colloidal particles will appear white or yellow?

(3) **COLOR** The degree of dispersion, i.e., the fineness of the particles, determines the color of many colloids. Upon addition of a few drops of acid to a very dilute solution of sodium thiosulfate ("hypo") it is possible to observe after a few minutes a white colloidal sulfur, and then, after some time, as more free sulfur is formed, the color changes to yellow as the larger particles begin to precipitate (Fig. 8). Likewise, it is the colloidal material in the sky and in lakes reflecting and refracting the light rays that causes the blue color.

(4) **CHARGED PARTICLES** Practically all colloidal particles in suspension are electrically charged. It is important to note that all of the particles of a given colloid will be charged positively or negatively. Consequently, the particles of a positive colloid attract those of a negative colloid and cause precipitation. The charges on a few common colloids are shown in the following table.

<i>Positive</i>	<i>Negative</i>
Albumin Hemoglobin Hydroxide of Fe, Cu, Al Colloidal Pb, Fe, Cu	Starch Mucilage Silver chloride Silicic acid Oil emulsion Indigo Prussian blue Most powders like charcoal and kaolin

Protein molecules, because of their comparatively enormous sizes, do not form true solutions, but instead behave as colloids when properly dispersed. For each dispersed protein there is a point of hydrogen ion concentration (pH, see p. 163) of the dispersing medium at which the particles of the protein will move neither to the anode nor to the cathode when placed in an electric field. This particular hydrogen ion concentration, expressed as a pH, is the *isoelectric point* of the protein in question. At this point the protein manifests minimum dissociation and dispersibility. Proteins are positively charged when dispersed in media more acid than their isoelectric points, and negatively charged in media less acid (more alkaline) than their isoelectric points. Therefore, the protein of egg albumin, which is negatively charged in alkaline



medium, will be precipitated upon the addition of a mercuric salt, the mercury providing positively charged ions.

Since all of the dispersed particles of a given colloid carry the same sign of charge they repel, and consequently a better dispersion and a more stable colloid are the result. This explains why the addition of certain colloids to some of the medicinal preparations, such as the use of dextrin in the preparation of Petrogalar and emulsions of cod liver oil, gives more stable colloids.

(5) **ADSORPTION:** One of the most characteristic and interesting properties of colloids is their ability to take up other substances (crystalloids or colloids) on their surfaces by a process called *adsorption*. It has been estimated that 1 ml. of solid material, when subdivided into particles of colloidal size, presents a total surface area of nearly 6,000,000 sq. cm. This property of the enormous total surface area of matter in the colloidal state of division is utilized in carbon-containing gas masks for adsorbing poisonous gases. It is this same property which accounts for the use of charcoal tablets in cases of indigestion. Gases and offensive odors are readily adsorbed by activated carbon and other colloids. Another good example of the adsorbing power of colloids is in the natural purification of water. The colloids of the soil retain the organic matter and the bacteria, and leave the water which drains through the soil pure enough to drink.



Fig 9—Adsorption. Surface adherence in the drying of one's face is an illustration of adsorption. Courtesy, H. Armstrong Roberts, Philadelphia

The preparation of certain medicines is independent upon this property of adsorption, for example, some drugs which are insoluble in water can be dispersed in the presence of starch. The particles of the drug adsorb starch, and the starch then functions as a protective colloid.

### Gels:

It has already been mentioned that many hydrophilic colloids can be prepared as gels, sometimes called jells or jellies. The dispersing liquid is retained by the colloid in much the same way that a sponge holds water. Freshly prepared soap is a colloid which has retained much water. A 1 per cent dispersion of gelatin in water will set to a semisolid. Some minerals, such as opals and agates, are dried jellies. Another example is pectin, a colloidal type of carbohydrate found in unripe fruit, which serves to form the supporting structure in making food jellies. In our homes we have seen these gels in custards, and in cornstarch and gelatin desserts. Frequently, gels, for example custards, will shrink upon standing and squeeze out a part of the liquid, a process called *syneresis*. The drying of a blood clot (gel) with the discharge of serum is an example of syneresis. It must not be thought that water is the only liquid used for the dispersion of colloidal matter. The alcohol and glycerin used by the pharmacist and the cosmetician are examples of other liquids employed in the preparation of many colloidal dispersions and gels.

Many of the tissues of the body are highly hydrated and should be considered as gels. The protoplasm, which is the fundamental material of the cell, is colloidal and exists as a gel (Fig. 10). The



Fig. 10—Protoplasm Is a Gel. The colloid protoplasm exists as a gel in the cells of the body. Why is the body able to hold so much water?

high degree of hydration of the colloidal substances in the cell accounts in large part for the fact that two-thirds of the weight of the body is water. Even the enzymes (*en'-zims*) which function as catalysts in body chemistry are colloidal in character.

As stated, the proteins, which constitute the greater part of the tissues, possess the property of taking up water \* This phenomenon is called *imbibition* (just the opposite of *syneresis*) Especially is this evident in the presence of acids and bases Consequently, in diseased conditions of the body when acids are formed the tissues "swell" or adsorb an abnormal amount of water In the action of a muscle the lactic acid which is produced stimulates changes in the water content It is only when the lactic acid is removed that the muscle fiber returns to normal Any local accumulation of acid in the tissues, such as resulting from a bee sting, causes excessive adsorption of water, thereby producing swelling or local edema

The importance of colloid chemistry is better appreciated when we learn that animal and plant tissues are colloidal in structure that our food passes into colloidal condition, and that colloid chemistry is closely related to cooking, baking dyeing, and sewage disposal In some areas of study and research we are just beginning to realize and appreciate the far reaching implications and applications of this branch of chemistry

## V. EMULSIONS

If water and a little oil, two substances that do not mix, are shaken together, small globules of the one remain suspended in the other for some time, and the result is a liquid, milky in appearance This kind of dispersion is called an *emulsion* However, the two liquids soon separate If a colloidal substance insoluble in both of the liquids is added before shaking, a more permanent emulsion results The insoluble colloid, called an *emulsifying agent*, here acts as a protecting colloidal agent, *i. e.*, it forms films around the oil droplets, which prevent them from running together A few drops of a soap solution will make a permanent emulsion of oil and water Salad dressing, for example, mayonnaise, is an emulsion of olive oil and vinegar, made permanent by the colloidal yolk of an egg Milk is an emulsion of butter fat in water, with albumin and casein serving as the emulsifying agent An emulsion of cod liver oil is often used medicinally

The emulsification of the fats in foods by the bile is of great physiological importance since this aids digestion Carron oil, which is used for burns, is an emulsion of linseed oil and lime-water

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\* Within recent years the water adsorbed by proteins and other classes of compounds as an integral part of tissue has been referred to as *bound water* It has a special significance in resisting desiccation

The oil is soothing, while the limewater neutralizes the acid formed when the skin is burned. Burns are dangerous because of the loss of proteins by oozing from the burned area and the destruction of the tissues to form poisons which enter the general circulation (See page 779)

### SELF-TESTING QUESTIONS

- 19 What is a suspension?
- 20 What does colloidal chemistry deal with?
- 21 Why do colloids have special properties?
- 22 What four characteristic properties do all colloids possess?
- 23 Define and illustrate dialysis.
- 24 What is a crystalloid?
- 25 Why are colloids used in many pharmaceutical preparations?
- 26 What is a gel?
- 27 What is an emulsion?
- 28 How are emulsions made permanent?

### SUGGESTED ACTIVITIES

#### I THOUGHT PROVOKING QUESTIONS

- 1 How does a solution compare in composition with mixtures and compounds?
- 2 What is the necessity of drinking water?
- 3 The boiling of meat to make broth is based upon what facts?
- 4 Why should a physiological saline solution be made correctly from an osmotic standpoint?
- 5 Given an apparent solution how could you prove whether it was a true solution or a colloidal dispersion?
- 6 In what ways are solutions important?
- 7 What is the difference between osmosis and dialysis?
- 8 How are emulsions made permanent? Explain using an example.
- 9 From a colloidal standpoint explain the preparation of cake frosting.
- 10 How are the properties of a liquid modified by dissolving a substance in it?
- 11 Explain the reason why a dried prune when placed in water gradually swells to the original size of the fresh fruit.
- 12 Would there be a difference between dead and living membranes with regard to the extent of osmosis? Illustrate.
- 13 In boiling meats why does the addition of a little acid such as vinegar or tomato juice make them more tender?
- 14 How would you expect colloidal dispersions to differ from true solutions in respect to osmotic pressure?
- 15 In what respect may blood be considered to be a solution? May it be considered to be a colloid? Explain.
- 16 Why does a chemist prefer solutions made up on a molar or normal basis rather than on a percentage basis?

- 17 One liter of a normal saline ( $\text{NaCl}$ ) solution contains how many grams of salt? How many times stronger is this solution than a physiological saline solution?
- 18 One liter of 0.5M hydrochloric acid contains how many grams of hydrochloric acid?

## II VOCABULARY TESTING OF NEW TERMS

solution	semipermeable	colloid	adsorb
solvent	isotonic	colloidal	gel
solute	hypertonic	dispersion	imbibition
dilute	hypotonic	peptization	emulsion
concentrated	hemolysis	dialysis	physiological saline
saturated	lysed	crystalloid	solution
supersaturated	plasmolysis	isoelectric	syneresis
osmosis	suspension	hydrophilic	hydrophobic

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 How Soil Purifies Water
- 2 The Importance of Osmosis in Plant Life and Growth
- 3 Some Solutions Commonly Used in Hospitals

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 659-663

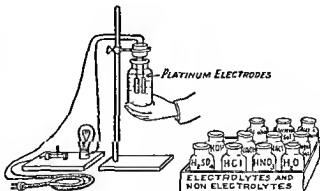
# IONIZATION—THE EXPLANATION OF CHEMICAL ACTION IN SOLUTION

## CHAPTER OUTLINE

- |  |   |
|--|---|
| <p><b>I. SOLUTIONS CONDUCTING ELECTRICITY</b></p> <p>(e) Testing conductivity of solutions</p> <p>(b) Acids, bases, and salts—electrolytes</p> <p>(c) Effect of dissolved substances on the freezing point, boiling point, and on osmotic pressure</p> <p><b>II. IONIZATION THEORY</b></p> <p>(a) Ions</p> <p>(b) Chemical activity of electrolytes</p> <p><b>III. ELECTRON EXPLANATION OF IONIZATION</b></p> <p>(a) Crystals contain ions</p> <p>(b) Difference between ions and atoms</p> <p>(c) Ionization is represented by reversible reactions</p> <p>(d) Why nonelectrolytes are non-conductors</p> | <p>(e) Ionization explains electrolysis</p> <p><b>IV. CHEMICAL ACTION IN SOLUTION</b></p> <p>(a) Effect of dilution on ionization</p> <p>(b) Strong vs weak acids</p> <p>(c) Strong vs concentrated acids</p> <p>(d) Ionization in the fluids of the body</p> <p>(e) Newer concept of acids and bases</p> <p><b>V. IONIC REACTIONS</b></p> <p>(a) Tests for ions</p> <p>(b) Preparation of an insoluble substance</p> <p>(c) Reactions which go to completion</p> <p>(d) Value of the ionic theory</p> <p><b>VI. STAINS</b></p> <p>(a) Stain removal methods</p> <p>(b) Stain removal</p> <p>(c) Wet and dry cleaning</p> <p>(d) Ousting the clothes moth</p> |
|--|---|

**Fig 1—Testing for Conductivity.** Apparatus for testing the conductivity of a solution

**NOTE.**—If dry cells are used as a source of current an ammeter will be found to be more sensitive than an incandescent lamp to small currents. Why are the electrodes usually made of platinum?



## I. SOLUTIONS CONDUCTING ELECTRICITY

### Testing Conductivity of Solutions:

When two copper wires leading from the positive (anode) and negative (cathode) terminals of a battery are connected, an electric current flows through the circuit thus made. If an incandescent

lamp is connected into this circuit, the glowing of the lamp indicates that a current is passing through the circuit. With this arrangement it is possible to test the conductivity of various solutions (see Fig. 1). If the two electrodes (terminals of the wires) leading from the battery are placed in distilled water and in solutions of such diverse compounds as salt, hydrochloric acid, sodium hydroxide, alcohol, and sugar, the lamp in the circuit will burn brilliantly in the solutions of salt, hydrochloric acid, and sodium hydroxide, but it will not light in the distilled water, in the solution of alcohol, or in the solution of sugar in water. This means that the solutions of salt, hydrochloric acid, and sodium hydroxide are good conductors of electricity. Before any deductions are made from these experiments attention should be called to the fact that as the current is passing through these latter solutions, bubbles of gas are being formed. This is an indication that some chemical change is taking place. A change of such a nature involving the decomposition of a substance by means of the electric current is called *electrolysis*.

### Acids, Bases, and Salts—Electrolytes.

From these experiments we learn that solutions of different substances in water vary in their power to conduct an electric current. Substances which conduct an electric current are called *electrolytes* (Greek *electron*, electricity + *lysin*, a splitting = electric splitting), while those which do not carry a current, such as sugar, are called *nonelectrolytes*.

<i>Electrolytes</i> (Conductors)	<i>Nonelectrolytes</i> (Nonconductors)
Acids Bases Salts	Pure Water Alcohol Sugar

Since the fluids of the human body contain acids, bases, and salts, it may be readily understood why it is dangerous to come in contact with any source of electric current. If one stands in water, or even in a damp place and makes contact with some source of electricity, such as an electric switch, or the handle of an electric iron, it is often possible to get a "shock." This shock is due to the electricity which passes through the solution of electrolytes in the human body and then by way of the minerals in the water to the ground.

An interesting and practical application of the conductivity of electrolytes in body solutions is the use of the electrocardiograph (Fig. 2), an instrument used by the physician for measuring variations in the electric current released during the contraction and relaxation of the heart.

To obtain a record of such a feeble current it is necessary to make a very close contact between the body and the instrument. This is obtained most commonly by using an electrode jelly (salt, powdered



Fig 2—Ionization Makes This Possible. A direct-writing electrocardiograph, which produces an immediate record of the heart's action for the physician, eliminating darkness both and delay, hitherto necessary on the old-type photographic electrocardiographs. What importance is attached to variations in the cardiac cycle? Courtesy, Sanborn Company.



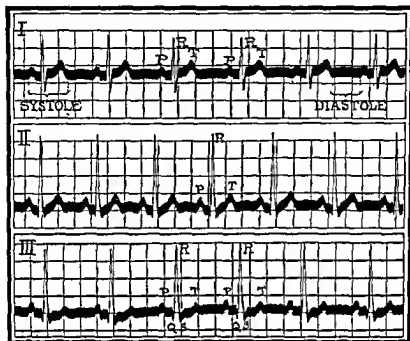


Fig 3—Normal Human Electrocardiogram. Waves are seen only during systole, when either the atria or the ventricles are contracting; when the heart is quiescent in diastole, waves are absent. The record consists of 3 parts or more called "leads." The patient's right hand, left hand, and left foot are connected with the instrument by separate wires, which are used successively in pairs. Lead I, Right hand and left hand. Lead II, Right hand and left foot. Lead III, Left hand and left foot. Leads II and III are the most common, but the chest leads are also very widely used. The three resulting tracings differ in various details, and their comparison adds certain refinements to electrocardiographic diagnosis. (From Jung & Earle *Anatomy and Physiology*, F. A. Davis Co.)

pumice, gum, etc.) between the electrodes placed over an artery on each arm and left leg, or various positions on the chest, neck, etc.

The purpose of the discussion thus far in this chapter has been to point out that one class of dissolved substances (nonelectrolytes) does not conduct an electric current, while the other large class of soluble compounds (electrolytes) does allow electricity to pass through its solutions.

### Effect of Dissolved Substances on the Freezing Point, Boiling Point, and on Osmotic Pressure:

We have learned in the preceding chapter that substances like sugar and salt, when dissolved in water, will lower the freezing

point and raise the boiling point of the water. Experiment has shown that the magnitude of the freezing point depression and the boiling point elevation is directly proportional to the number of solute particles in a given quantity of solvent. Osmotic pressure values are similarly dependent upon the concentration of solute particles. As an example, 10 grams of sugar dissolved in 1000 grams of water will produce twice as much change in the freezing point, boiling point, and osmotic pressure as 5 grams of sugar in the same quantity of water.

All nonvolatile nonelectrolytes are equally effective. Cane sugar ( $C_{12}H_{22}O_{11}$ ), glycerin ( $C_3H_8O_3$ ), and urea ( $CO(NH_2)_2$ ) are non-electrolytes and have gram molecular weights of 342 grams, 92 grams, and 60 grams respectively. If one prepares solutions by dissolving a gram molecular weight (one mole) of each of these nonelectrolytes in 1000 grams of water, it will be found that for all three the freezing point of the water is depressed by the same amount, namely  $1.85^\circ C$ . Also, the boiling point of the water is elevated by  $0.52^\circ C$ , and the osmotic pressures developed by the solutions are the same. The reason for this identical behavior of the nonelectrolytes becomes clear from Avogadro's law, which states that gram molecular weights of all nonelectrolytes contain the same number of molecules. Notice that these effects do not depend upon the kind of dissolved particles, or upon their weight, but only upon the number of particles. Thus 342 grams of cane sugar (one mole) and 60 grams of urea (one mole) contain the same number of molecules.

In the case of electrolytes, when compared to nonelectrolytes, the changes produced in the freezing point and the boiling point of water are more marked. Thus, a gram formula weight (one mole) of sodium chloride, 58.5 grams, when dissolved in 1000 grams of water, lowers the freezing point and elevates the boiling point by amounts almost twice those produced by nonelectrolytes. In order to explain the abnormal behavior of electrolytes in solution, as compared to nonelectrolytes, and to account as well for a number of other important properties of electrolytes, for example, electrical conductivity, an ionization theory has been developed.

### SELF-TESTING QUESTIONS

1. What is an electrolyte?
2. What classes of substances are electrolytes?
3. Why may you get an electric shock?

- 4 How is common salt used in electrocardiograph work?
- 5 What three effects in the properties of solutions are produced by dissolved substances?
- 6 A change in the properties of a solution of a nonelectrolyte is due to what?
- 7 What is a gram molecular weight?

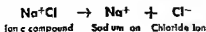
## II. IONIZATION THEORY

### Ions

It has been pointed out that all nonelectrolytes when used in the same concentrations have the same effect in depressing the freezing point and elevating the boiling point of water, and in developing osmotic pressures. Also, the magnitudes of these effects are determined solely by the number of particles in solution. Since electrolytes produce greater changes than nonelectrolytes, it is evident that one gram formula weight (one mole) of an electrolyte must provide a greater number of particles than does one gram formula weight (one mole) of a nonelectrolyte.

Sodium chloride,  $\text{NaCl}$ , is a typical electrolyte, and it has been already stated that this substance is an ionic compound, i. e., the fundamental particles of structure are sodium ions and chloride ions. Therefore, a water solution of sodium chloride contains no molecules of the salt, but, instead, wandering sodium ions and chloride ions are present. The total number of ions in one mole of sodium chloride is twice the number of molecules in one mole of any nonelectrolyte. If one dissolves one mole of sodium chloride in 1000 grams of water, it would be expected that the solution would freeze not at  $-1.85^\circ \text{C}$ , but at twice this value, or  $-3.7^\circ \text{C}$ . By experiment the freezing point is found to be  $-3.3^\circ \text{C}$ , not quite as low as to be expected. This is due to the fact that the ions, particularly in the more concentrated solutions, are not entirely free to act as individual, unhampered particles. The word *ion* is derived from the Greek language, and means "wanderer".

The following ionic equation brings out the fact that a gram formula weight of sodium chloride provides twice as many particles as a mole of any nonelectrolyte

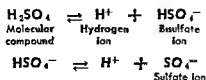


Sodium hydroxide, like sodium chloride, is an ionic compound



Sulfuric acid is a water solution of a molecular type of compound,

called hydrogen sulfate,  $\text{H}_2\text{SO}_4$ . In water this compound ionizes in two stages



The double arrow indicates that the reaction is reversible, i. e., two opposing processes are going on at the same time, and consequently both ions and molecules will be present as solute particles. Seldom do all of the molecules in solution dissociate into ions.

Ions are electrically charged particles, and may be charged atoms, or charged groups of atoms called radicals. The number of charges on an ion corresponds to its valence. It is the ions which carry the electric current between the poles, or electrodes, in solutions of electrolytes. Ions, regardless of type, have the same effect on the freezing point, boiling point, and osmotic pressure as do molecules. Notice again, it is the number of solute particles, not kind, that determines the magnitudes of these three properties of solutions.\*

### Chemical Activity of Electrolytes:

From the previous paragraphs it is to be noted that electrolytes are of two broad classes, those which in pure state are ionic compounds (sodium chloride, potassium nitrate, sodium hydroxide, etc.), and those which are molecular in character, but which dissociate to varying degrees in water to give ions. For the latter it must be understood that the ionization is caused by the solvent, usually water, and not by the electric current. The discussion at the beginning of this chapter was used to show that some solutions conduct the electric current by reason of the ions moving in an orderly direction between the two electrodes. Some molecular compounds ionize more completely than others, and water is considered the best ionizing solvent. In a concentrated solution the molecules of such an electrolyte are close together and unable to dissociate into a great many ions because there is always a tendency of the ions to unite and form molecules. Consequently, dilution aids ionization up to a certain point because in dilute solutions the ions meet each other less frequently as they wander about and are

\* The extent of ionization depends not only on the solution but also upon the physical state. For example, melted  $\text{NaCl}$ , but not solid  $\text{NaCl}$ , can be electrolyzed. The temperature also affects ionization, since some gases are ionized at high temperatures.

less apt to unite to form molecules. Since *chemical reaction is greater between ions than molecules* dilute solutions bring about chemical changes more rapidly and completely. Many compounds which ionize readily in water do not ionize when dissolved in other liquids.

From a physiological standpoint the action of the different ions is of great importance in the life processes of the body. It is the ions of dissolved electrolytes that produce osmotic pressure in the cells and thereby regulate body functions. In the blood it is the ions of calcium on the one hand, and the ions of sodium and potassium on the other, which account for the contracting and relaxing of the heart muscle. The general functions of inorganic ions in the living body tissues are to (1) contribute to the building and repair of tissues, (2) influence the contraction of muscles and irritability of nerves, (3) help maintain the osmotic conditions, (4) be largely responsible for the *acidity and alkalinity* of digestive juices, and (5) insure normal chemical reactions.

### SELF-TESTING QUESTIONS

- 8 What is an ion?
- 9 How does the electric charge on an ion compare with its valence?
- 10 What produces the freely moving ions?
- 11 How does the effect produced by a molecule in solution compare with the effect produced by an ion in solution?
- 12 Why is it generally better to work with a dilute solution?
- 13 Illustrate by an example the meaning of a nondissociating liquid.
- 14 In solutions of electrolytes what are the reacting particles?
- 15 What are the various functions of the ions in the body cells?

## III ELECTRON EXPLANATION OF IONIZATION

### Crystals Contain Ions

How does the electron theory explain the formation of the ions of sodium chloride? From a study of the original atoms of sodium and chlorine (Fig. 4) it may be noticed that when the outer shell, or

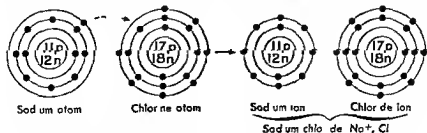


Fig. 4—Formation of Sodium Chloride. Eight electrons in the outer shell produce a satisfied or stable condition.

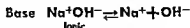
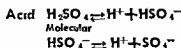
valence electron, of the *sodium* atom moves over to the chlorine atom, the sodium atom is left with an extra positive charge and consequently becomes a sodium ion,  $\text{Na}^+$ . At the same time, the gain of an electron by chlorine makes the chlorine atom become a chloride ion,  $\text{Cl}^-$ . The sodium chloride formed has a stable electron structure, there being eight electrons in the outer shell of each ion. Compounds like sodium chloride formed by an exchange of electrons are often called ionic compounds. From this it is evident that crystalline sodium chloride is in reality made up of sodium ions and chloride ions, which are held together by their electrical attraction. This type of valence holding the ions of electrolytes together is called *electrovalence*. Similarly, all crystalline electrolytes are composed of ions, and therefore it is not necessary to dissolve crystals to get ions. It is only when crystals are dissolved in some dissociating liquid as water, or melted, that the valence forces are overcome, and the ions are free to move about.

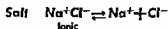
### Difference between Ions and Atoms:

As just stated, when the outer shell of an element is completed, that is, when there is no tendency to lose or gain electrons, the atom becomes stable. In other words, chemical activity is then greatly reduced. Examination of the diagram of the sodium ion shows that a stable condition of eight electrons exists in the outer shell. This may explain why the sodium ions are inactive in water, transparent, and nonpoisonous, while the sodium atoms react vigorously with water, and are poisonous. At first thought, it is hard to understand why the properties of an atom differ so much from the properties of an ion. However, the chemical activity of an element is measured in terms of the ability of its atoms to gain, lose, or share electrons. Chlorine, for example, is reactive because each of its atoms has a great affinity for an electron to complete and stabilize the outer shell.

### Ionization Is Represented by Reversible Reactions:

We may now have some idea of the behavior of an electrolyte when in solution. The following equations show the ionization or the dissociation of typical acids, bases, and salts.





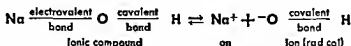
The double arrows in the first two equations indicate that the different kinds of ions reunite when water is removed. Not all of the molecules ionize and consequently there are both positive and negative ions and undissociated molecules present. As the ions and molecules move about in solution some of the positive and negative ions unite to form molecules, while other molecules are dissociating into ions. Soon, however, an equilibrium is reached, and the percentage of ions and molecules in the solution remains constant. Such reactions, which can go in either direction at the same time, are called *reversible* reactions. It will be noticed again that the number of electric charges an ion bears is the same as the valence. Also, it is noticeable that some compounds, like  $\text{H}_2\text{SO}_4$ , form more than two ions, and ionize in stages.

Both sodium hydroxide ( $\text{NaOH}$ ) and sodium chloride ( $\text{NaCl}$ ) are ionic compounds. In water the ions of these crystalline solids are pulled apart and become free to move about. Occasionally, particularly in the more concentrated solutions, ions of opposite charge collide and form what might be called a "cluster" of ions. In the examples used here the simplest clusters would be  $(\text{Na}^+, \text{Cl}^-)$  and  $(\text{Na}^+, \text{OH}^-)$ . In the clusters the charges become more or less satisfied; hence in this form the ions have a reduced chemical activity. In equations of ionization, where the solute is an ionic compound, the double arrow signifies equilibrium between free ions and ion clusters.

### Why Nonelectrolytes Are Nonconductors.

The question might well be asked, "Why do nonelectrolytes not ionize?" Thus far in this chapter we have been concerned with loss or gain of electrons to give ions. Atoms can also share electrons with each other, so that both acquire complete outer shells. It has been stated repeatedly that several gaseous elements exist as two atoms per molecule ( $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{Cl}_2$ , etc.). In the case of the chlorine molecule (Fig. 15, p. 30), each of the two atoms shares one of its electrons with the other, and in that way completes the orbit of each, thus forming a molecule of chlorine. This type of valence holding the atoms of nonelectrolytes together is called *covalence*, and the compounds are known as *covalent* compounds.

The atoms of a compound radical are held together by covalence, and consequently radicals do not separate into individual ions as can be noticed in the case of sodium hydroxide.



When shared electrons belong as much to one atom of an element as another, it is impossible to form ions, consequently, we conclude that nonelectrolytes may dissolve, but not ionize, because of the sharing of electrons. This property of atoms of nonelectrolytes to share electrons further helps us understand why nonelectrolytes are chemically less active.

Since valence depends upon the number of electrons in the outer shell of the atom, a briefer method of showing shared electrons is to drop the inner shells, write the symbols of the atoms, and surround the symbol of each atom by paired dots. Each pair of dots then corresponds to the number of pairs of electrons shared, and each pair represents a valence of one. The chlorine atom is indicated as



The chlorine *molecule* which contains two atoms with the two atoms sharing a pair of electrons, and each atom having six unshared electrons to complete its orbit, is represented as



The diagrammatic formulas of the following nonelectrolytes,  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{CH}_3\text{OH}$  further show how shared electrons exist between the respective atoms of covalent compounds



The carbon atom in  $\text{CH}_4$  shares four pairs of electrons with the four H atoms to form a molecule of methane, and has a valence of four.



The carbon atom in  $\text{CO}_2$  shares four pairs of electrons with the two atoms of oxygen to make a molecule of carbon dioxide.



The carbon atom in  $\text{CH}_3\text{OH}$  shares four pairs of electrons, three with the three H atoms and one with the O atom. Another pair is shared between the O atom and the H atom attached to it.

It must not be concluded that all of the molecular structures which result from atoms sharing electrons are nonelectrolytes.





In a like manner the negatively charged  $\text{OH}^-$  and  $\text{Cl}^-$  are attracted to the anode (positive electrode) where the chloride ion which is the more easily discharged of these anions gives up an electron to form a chlorine atom:



The union of chlorine atoms forms molecules of chlorine; these then dissolve in the solution to some extent, but largely escape as a gas.



The accumulation of  $\text{Na}^+$  and  $\text{OH}^-$  in the solution as the electrolysis progresses provides sodium hydroxide (lye) which is another product of the electrolysis of sodium chloride solution. The electrolytic process which has been described is an important commercial method for the manufacture of chlorine and sodium hydroxide. The hydrogen which is produced may be burned in the chlorine to obtain hydrogen chloride for the preparation of hydrochloric acid.

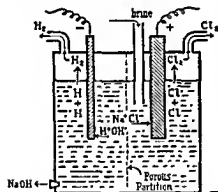
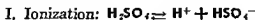
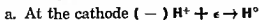


Fig. 5—Electrolysis of Brine. Diagram illustrating the theory of electrolysis of an  $\text{NaCl}$  solution. What three important products are obtained?

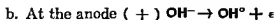
Other examples of equations for ionization and electrolysis follow:



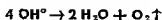
II. Electrolysis of water which contains a little sulfuric acid:



then



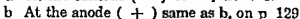
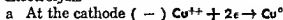
then



The hydroxyl ion is more readily discharged than the sulfate ion hence in the electrolysis of extremely dilute sulfuric acid only water is decomposed



II Electrolysis



In the electrolysis of copper sulfate solution, the copper deposits on the cathode. If copper electrodes are used copper is taken from the anode into solution as copper ion



This transfer of copper metal from the anode via the solution to the cathode explains the general principle involved in *electroplating*, and *electrorefining* of copper

From the foregoing explanations it is evident that *electrolysis* is a process in which an electrolyte in solution is chemically changed by the energy of the electric current

### SELF-TESTING QUESTIONS

- 16 What is a valence electron?
- 17 What is a stable electron structure?
- 18 Are ions present in crystalline compounds?
- 19 What two conditions will liberate ions of an electrolyte?
- 20 When is an element inactive?
- 21 How can you account for the difference in the properties of an atom and an ion? What is a reversible reaction?
- 22 In chemical reactions when do atoms form covalent compounds?
- 23 Why do not some compounds ionize?
- 24 Why are certain covalent compounds not very active in solution?
- 25 What is the meaning of pair of electrons shared?
- 26 Why do molecules like HCl form ions in water solution?
- 27 Explain the electrolysis of sodium chloride
- 28 What is electroplating?
- 29 Explain the electroplating of copper by use of the ionization theory

## IV CHEMICAL ACTION IN SOLUTION

### Effect of Dilution on Ionization

As has been noted, the greater the number of ions present, the better the solution will conduct the electric current. If we start with a fairly concentrated solution of a molecular compound which is capable of ionizing and begin to dilute the solution we find that the conductivity increases up to a certain point. This means that

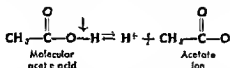
in fairly concentrated solutions only a part of the molecules are dissociated into ions, but with increasing dilution more and more of the molecules ionize. Of course, a point is reached where further dilution produces no more ions since there are no more molecules to ionize. For solutions of ionic compounds, where there are no molecules, the ions interfere with one another in the more concentrated solutions. As the solutions are diluted the ions act more and more independently. In general, compounds react better in dilute than in concentrated solution as evidenced by the fact that concentrated sulfuric acid has but little effect upon zinc until the acid is diluted with water. Dilution and consequent ionization overcomes the slow reaction rate. The effect of dilution may also be shown by the following experiment. Place a small amount of soap powder or shavings in a tall graduated cylinder (1000 ml). Cover with about 100 ml of alcohol, add a few ml of phenolphthalein indicator, and shake for several minutes in order to dissolve some of the soap. The indicator always turns red in the presence of hydroxyl ions ( $\text{OH}^-$ ), which are not in evidence at this stage of the experiment. Add water in 100 ml amounts, shaking well after each addition. Soon a faint pink color predominates, showing that with increasing dilution the molecules of the soap, which first dissolved, are beginning to produce hydroxyl ions through their hydrolysis. The color deepens and deepens with increasing dilution until a red color is produced.

Again to illustrate the effect of dilution on ionization, we find that glacial acetic acid does not conduct the electric current, but if the acid is diluted with water the current will flow through, showing that dilution produces ionization and therefore conductivity.

### Strong vs. Weak Acids-

In the following chapter it will be shown that all acids produce hydrogen ions in solution, a fact which accounts for the sour taste and other characteristic properties of acids. From this fact, by application of the ionization theory, it is evident that the greater the number of  $\text{H}^+$  ions in solution the more pronounced are the acid properties. The common acids,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ , ionize more than other acids and are, therefore, called strong acids. In other words, *strength means the degree of ionization* whether applied to acids or bases. Acids, like carbonic ( $\text{H}_2\text{CO}_3$ ), acetic ( $\text{H}-\text{C}_2\text{H}_3\text{O}_2$ ), and boric, ( $\text{H}_3\text{BO}_3$ ), are weak in comparison to the above mentioned common acids, because they do not ionize to any great extent to

release hydrogen ions. In fact, we use dilute acetic acid (4 per cent) as a vinegar in our foods, citric acid in lemonade, carbonic acid as soda water, and boric acid as an eyewash. There are many compounds like acetic acid, the water solutions of which do not contain many ions. The molecules of such compounds are *mostly covalent*, that is, they contain shared electrons between the atoms, only an occasional electron being gained or lost where there is an inequality of sharing. Thus, in the partially structural formula of acetic acid,



all bonds, except the one indicated by the vertical arrow, are strictly covalent. The bond identified by the arrow, however, has some electrovalent character. This means that occasionally a molecule of acetic acid ionizes at the point indicated to give hydrogen ion and the negative acetate ion. In many cases where there is not sufficient solubility the concentration of ions will necessarily be low, and such compounds are weak and inactive chemically.

### Strong vs Concentrated Acids

Often the term "strong acid" is used when the term "concentrated acid" should be employed. Strength refers to the percentage of free  $\text{H}^+$  ions and not to the concentration of the acid molecules, which are generally inactive. The most concentrated acid has the least amount of water present, and, therefore, cannot have many  $\text{H}^+$  ions present. Concentrated sulfuric acid usually contains 95 per cent of  $\text{H}_2\text{SO}_4$ , while concentrated hydrochloric acid contains about 37 per cent of  $\text{HCl}$ . The sulfuric acid, then, is the more concentrated, while the hydrochloric acid is the stronger of the two in that it has a higher concentration of free hydrogen ions. Just as there are strong and weak acids, so there are strong and weak bases, the strengths of bases being determined by the concentration of  $\text{OH}^-$  ions. A comparison of the degree of ionization of acids of the same molecular concentration (1/10 normal\*) is shown in the following table.

\* Normal acid solution contains one gram equivalent of hydrogen per liter.

Under the same conditions, 100 molecules of

Hydrochloric acid ( $H^+$ , $Cl^-$ )...	..will yield 92.	H ions.
Nitric acid ( $H^+$ , $NO_3^-$ )... ..	" " 92.	" "
Sulfuric acid ( $H^+$ , $HSO_4^-$ ) . . . .	" " 61.	" "
Sulfurous acid ( $H^+$ , $HSO_3^-$ )	" " 40.	" "
Acetic acid ( $H^+$ , $C_2H_3O_2^-$ )	" " 13	" "
Carbonic acid ( $H^+$ , $HCO_3^-$ ) .	" " 0.17	" "
Hydrosulfuric acid ( $H^+$ , $HS^-$ )	" " 0.07	" "
Boric acid ( $H^+$ , $H_2BO_3^-$ ) . .	" " 0.01	" "

Since practically all salts are ionic compounds, we do not speak of salts as strong or weak. Most soluble salts show a high concentration of free ions, the percentage in a N/10 (1/10 normal) solution ranging from 65 per cent to 85 per cent.

<i>Types of Salts</i>	<i>Per cent of Dissociation (free ions) in N/10 Solution</i>
$M^{+1}A^{-1}$ (e.g., $NaCl$ )	85 to 86
$M^{+2}A^{-1}$ (e.g., $BaCl_2$ )	72 to 77
$M_2^{+1}A^{-2}$ (e.g., $Na_2SO_4$ )	70 to 73
$M^{+2}A^{-2}$ (e.g., $MgSO_4$ )	50 to less

### **Ionization in the Fluids of the Body:**

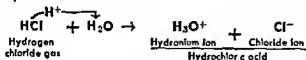
The ionization of solutions of acids, bases, and salts in the alimentary tract is illustrated by poisoning from bichloride of mercury. The water passes by osmosis from the tissues, dilutes the bichloride, causes more ions to be formed, and thereby hastens the chemical action in the tissues. Since ionization increases with dilution, a small dose of a poison is dissolved, ionized, and more quickly absorbed than an overdose. All metallic ions are quickly absorbed but slowly excreted, as most of them form insoluble compounds with the protoplasm. Lead acetate forms an insoluble protoplasmic compound, and for this reason it is used as an astringent. Salts of sodium, potassium, calcium, and magnesium are normal constituents of the fluids in the body and are therefore much used in medicines. They are seldom toxic and excretion is more rapid than absorption.

### **A Newer Concept of Acids and Bases:**

In the theory of ionization just presented, acids and bases in water furnish  $H^+$  and  $OH^-$  ions respectively, but Bronsted (1923)

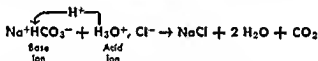
and his co workers found that acids and bases are active in *non aqueous solvents* in which they could not ionize. These discoveries have led to new definitions for acids and bases.

According to the Bronsted theory a proton ( $H^+$ ) never exists free in water or in other media, but combines with the solvent molecules. Thus with water the proton of an acid forms  $H_3O^+$ , called the hydronium ion, a hydrated hydrogen ion (usually represented as  $H^+$ )



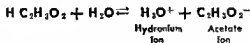
An acid is defined as a *proton donor*, strength being determined by the extent of proton transfer.

Conversely, a *base is a proton acceptor*. This means that many molecules, as  $H_2O$  and  $NH_3$ , and ions, such as  $OH^-$ ,  $O^{2-}$ ,  $S^{2-}$ ,  $CN^-$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $SO_3^{2-}$ , are bases.



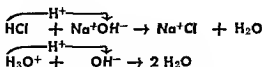
With this somewhat recent view of a proton ( $H^+$ ) the theory of ionization now is modified as follows.

1 Active acids ( $HCl$ ,  $H_2SO_4$ ) in water change almost instantly into ions, whereas moderately active acids ( $H_2SO_3$ ,  $H_3PO_4$ ), or slightly active acids ( $H_2CO_3$ ,  $HC_2H_3O_2$ ) are less completely ionized because their action with water is reversible. For example

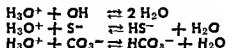


2 Active bases (the alkalis) and most salts are completely ionized even in the crystalline state since they consist of ions arranged alternately within the crystals. Consequently in aqueous solution or the melted state the crystals are broken down into freely moving ions. Thus in the process of dissolving, the ions of active bases provide hydroxyl ions ( $OH^-$ ) which are hydrated just as are the hydrogen ions ( $H^+$ ).

When metallic hydroxides as  $NaOH$ , are placed in acids, the proton transfers from acid molecules (or  $H_3O^+$  ions of dilute acids) to hydroxyl ions of the metallic hydroxide to form water, e.g.,



Neutralization then could be represented as follows



The main reason for denying the existence of  $H^+$  ions is that the electron theory indicates the hydrogen atom is composed of one proton and one electron, and in an ionization reaction it must lose an electron in order to have a positive charge. Therefore  $H^+$  ions must be protons moving independently in water solutions of acids. This is hard to believe. It seems more logical that the protons become attracted to water molecules, and experimental evidence now supports this newer concept.

Since Bronsted's concept of acids and bases has not been used consistently in general chemical literature it seems sufficient merely to introduce the theory at this time. Even though the activity of all acids is due to hydronium ions ( $\text{H}_3\text{O}^+$ ), for convenience we more often use  $\text{H}^+$  as a general symbol to measure any acid, and  $\text{OH}^-$  to represent any alkali.

## SELF-TESTING QUESTIONS

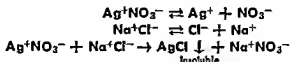
- 30 What is the effect of dilution upon ionization?
- 31 What is meant by a strong acid?
- 32 What is meant by a strong base?
- 33 Why are some acids or bases weak?
- 34 How does strength differ from concentration?

## V. IONIC REACTIONS

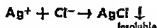
### Tests for ions:

Sometimes a student is required to make a test for substances in solution. Usually an *insoluble solid* is formed as a precipitate. Quite frequently a *recognizable gas is liberated*, and often a definite *color is produced*. To illustrate precipitation, suppose we wish to make a test for the chloride ion. The substance generally used for this test is a solution of silver nitrate, since it reacts with a soluble chloride to form white insoluble silver chloride.



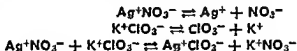


or simply,



### Preparation of an Insoluble Substance:

In the ionic reaction just discussed the silver chloride, being an insoluble solid, separates out of solution. We might have predicted that the silver ion and the chloride ion would have formed an insoluble substance if we had consulted the solubility table. If we turn to this table, page 778, and glance down the left vertical column we find Ag. Horizontally, to the right of Ag, we soon notice an I. Upon raising our eyes to the top of the vertical column containing this I we observe Cl. The I means insoluble, and therefore indicates that positive silver ions and negative chloride ions in the same solution would form an insoluble substance. A soluble silver salt then is used in testing for the chloride ion but not for the chlorine atom. For example, potassium chlorate contains the chlorine atom, but will not react with the silver ion to form silver chloride.



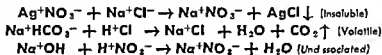
It will be further noticed in the solubility table that this compound,  $\text{AgClO}_3$ , is soluble as evidenced by the W which means water soluble. It is quite evident then that the solubility table serves as a means of indicating what combinations of ions will form soluble or insoluble substances. As a further aid in testing, it quite frequently happens that the insoluble substances formed are colored.

In a previous paragraph, it was stated that all acids have common properties, since they provide the common hydrogen ion. The color of many salt solutions is due to one of their common ions. For example, the green acid  $\text{CuCl}_2$ , or the dark brown solid  $\text{CuBr}_2$  in dilute solutions is blue, because of the common cupric ion  $\text{Cu}^{++}$ . So it is that any solution containing the same common ion ( $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$ , etc.) generally reacts in the same way and responds to certain specific tests.

## Reactions Which Go to Completion:

In some of the equations presented in this chapter the double arrow has been used to indicate that these reactions "work backward," i.e., they are reversible. Both the direct and reverse reactions continue simultaneously in a state of dynamic equilibrium.

For those reactions which go to completion, only one arrow is used in the equation, and pointed in the forward direction. Here one or more of the products formed must leave the field of the reaction as (1) insoluble (2) volatile or (3) un-ionized. Examples of these types are given in the following equations:



## Value of the Ionic Theory:

The theory of ionization is a practical aid in helping to explain many chemical reactions which take place in solutions of acids, bases, and salts. Thus far, the theory has given a fairly satisfactory explanation of the following facts:

- 1 The abnormal effect of electrolytes as compared to nonelectrolytes on the boiling point, freezing point, and the osmotic pressure of solutions
- 2 Electrolysis and electroplating
- 3 The greater chemical activity of electrolytes as compared with nonelectrolytes
- 4 Different strengths of acids and bases
- 5 Prediction of the behavior in solution of substances yielding a common ion

In addition to the above facts, advanced chapters will consider other important ionic reactions such as neutralization, replacements of metals by other metals, chemical reactions between electrolytes, and hydrolysis of salts.

## SELF-TESTING QUESTIONS

- 35 How can you usually tell whether you are getting a test for an ion?
- 36 How can you predict whether a reaction will form a precipitate?
- 37 Are precipitation tests used for ions or for atoms?
- 38 Why are dilute solutions of  $\text{CuSO}_4$ ,  $\text{CuCl}_2$ , and  $\text{CuBr}_2$  all blue?
- 39 The ionization theory is used to explain the reactions which take place between what classes of compounds?

- 40 When will reactions between ions take place?
- 41 What are five uses of the ionization theory?
- 42 What types of chemical reactions go to completion?
- 43 What is the nature of the reversible reaction?

## VI. STAINS

NOTE The remainder of this chapter may be omitted when time must be saved. It may be given as a reading assignment in conjunction with the laboratory exercise on stains.

### Stain Removal.

In the hospital, home, laundry, or dry cleaning establishments there are frequent demands made for the removal of stains, and especially so in connection with the general care of clothing. Although many of the methods employed demand special knowledge in the chemistry of textiles and stains, most stains may be removed effectively and inexpensively in the home if a few simple precautions are taken. Of all the rules to follow, the most important is prompt treatment of the stain, since upon prolonged exposure to the air, washing, ironing, or other factors, many stains undergo a chemical change to form stains that in some cases are almost impossible to remove without serious injury to the fabric. Stains of a physical nature, as grease or fresh paint, are of the class easily removed by selecting the correct solvent, but if on the other hand the stain has undergone a chemical change, as old ink stains, then a chemical must be used to change it back into a form that is soluble and which may be washed out. Most chemicals applied to fabrics have a tendency to weaken and destroy the fibers.

Just as in any ailment, we must first understand the nature of the trouble, so we must know the nature of the stain before proper treatment may be given. Trying out different chemical compounds upon stains of unknown composition may cause the stain to become more insoluble. For instance, such a simple and apparently harmless compound as hot water may be of great assistance in removing fresh ink, or most fruit stains, yet in the case of protein stains (milk, eggs, blood) hot water coagulates the albuminous material and makes it very difficult to remove. Also a failure to know the nature of the fabric and dyestuffs in many cases will result in a loss of the dyestuffs and injury to the goods. This is especially so in attempting to remove stains from material made of both animal and vegetable fiber, such as silk and cotton. Furthermore, there are many synthetic fabrics on the market, such as rayon or cellulose acetate, which certain chemicals (acetone, chloroform, acetic

acid, alkalies, bleaching agents) dissolve. Also, there are fabrics which contain certain amounts of weighted materials (tin compounds) which are very much affected by certain solvents. In view of the above statements, unless thoroughly familiar with the nature of the stain and the kind of fabric, as a rule, it will be more satisfactory to have the stains removed by a reliable dry cleaner who employs one or more "spotters" trained in this work.

### Stain Removal Methods:

The removal of stains, called "spotting jobs," consists of four types solvent, absorption, digestive, and chemical

(1) By the *solvent* type is meant the application of some solvent to the stain that will dissolve it from cloth. As an example of this type of solvent we refer to the removal of sugar spots by the use of water. Other solvents are acetone, ether, alcohol (wood or grain), carbon tetrachloride, trichloroethylene, and certain hydrocarbons such as naphtha, gasoline, and turpentine.

(2) The use of whitening on white shoes is a very good example of removing stains and dirt by absorption. Other absorbents are



Fig 6—Stain Removal Treating a stain with sodium perborate bleach. What other bleach solutions might be similarly used? Courtesy, U S Department of Agriculture

magnesium carbonate, fuller's earth, corn meal, and certain chalks ( $\text{CaCO}_3$ ,  $\text{MgO}$ ) In conjunction with this method, many stains insoluble in the fabric such as some lipsticks, mascara, and inks may be lubricated by applying an oil which carries or slides the insoluble pigment from the goods

(3) In the case of coagulated albuminous stains, it is often necessary to use enzymes or *digestive* agents which decompose protein into water soluble substances

(4) When the above methods are ineffective, certain chemical reagents must be used to change the insoluble stain into a soluble or colorless stain Such chemicals usually are bleaches chlorine, chlorine compounds, hydrogen peroxide, potassium permanganate, oxalic acid, sodium perborate, and hydrosulphites

From the foregoing it is evident that the spotter must know his textile, his dyes, and the effect of chemicals upon them

### Wet and Dry Cleaning:

In a few cases, more so in the South where there are more linen, flannel, and summer suits worn, there is some demand for wet cleaning Steam is seldom used since it may result in shrinkage and injury to many fabrics

By "dry cleaning" we mean the use of volatile organic solvents to the exclusion of water In the modern dry cleaning plants, the material is agitated in a closed drum with some volatile organic solvent as naphtha, benzine, trichloroethylene, or carbon tetrachloride (Carbona), the latter two solvents being the safest since they are nonflammable Under the name of Stoddard Solvent, and various trade names, dry cleaning plants and homes are using an inexpensive petroleum distillate, which not only is free of objectionable odors, but also is almost nonflammable It is a reasonably safe solvent since its boiling point is above that of gasoline and below that of kerosene, and unless the temperature is very high there is not sufficient vapor to support a flame or cause an explosion When properly done, dry cleaning generally restores silk, wool, and synthetic fabrics to their original condition without the dangers of loss of shape, texture, or drape As a rule, not only is all of the soil and grease removed, but also germs and insect life are killed If for no other reason than the latter, dry cleaning should be a general rather than an occasional practice Very few people realize and appreciate the importance of dry cleaning from the standpoint of health

When a solvent such as naphtha, trichloroethylene, or Carbona is used on a piece of cloth to remove a stain such as grease, the grease is dissolved by the reagent and is spread as far as the liquid penetrates the goods. The solvent upon evaporation leaves such a thin layer of grease that it is not perceptible on rough woolen goods. Of course, some may be removed by penetrating the cloth used in rubbing the grease spot. On the other hand, when used on thin silk goods, the tendency is simply to enlarge the spot and leave a ring of grease after evaporation of the solvent. From this it is evident that to thoroughly remove the grease, the goods must be rinsed repeatedly in fresh solvent. This is the method used in dry cleaning establishments.

### Ousting the Clothes Moth.

In the early days the common procedure against clothes moths was to use moth balls, formerly of camphor, now of naphthalene. The best either substance did was to prevent moths from laying eggs on stored material.

Paradichlorobenzene, commonly called dichloride, ushered in a new era of clothes moth control since for the first time there was available a handy crystalline material that not only would keep clothes moths away but also would slowly kill the eggs and larvae. A half pound or more of the crystals placed on the highest shelf in clothes closets will protect clean fabrics. Furs though are kept more safely in cold storage where at a temperature below 40°F the young larvae are inactive and cannot survive many weeks.

If moths have become entrenched then they must be killed by some spray material such as DDT or chlordane.

Clothes frequently used, exposed to bright light or dry heat do not harbor moths. Garments should not be stored at home without first being dry cleaned, because soiled clothing attracts moths much more readily than clean clothing.

### SELF-TESTING QUESTIONS

- 44 Why should a fresh stain receive prompt treatment for removal?
- 45 Why should the nature of the stain be known before treatment?
- 46 State and explain the four general methods of removing stains.
- 47 How are clothes dry cleaned?
- 48 Why is it important to have suits, dresses, etc. dry cleaned even though such garments are not soiled from wearing?

## SUGGESTED ACTIVITIES

### I THOUGHT PROVOKING QUESTIONS

- 1 Why is salt thrown on icy sidewalks or on the ice in an ice cream freezer?
- 2 In sea bathing why do you not feel any electric shocks from the ions of salts?
- 3 What is the effect of substances dissolved in water with regard to the properties of the solution?
- 4 In what way can you account for the difference in the properties of electrolytes as compared to nonelectrolytes?
- 5 What facts led to the formation of the ionization theory?
- 6 Why are ions of chlorine not as active as the atoms or molecules of chlorine?
- 7 What is the effect of passing a current through a solution containing an electrolyte?
- 8 Explain your distinction between a molecule, an atom, and an ion of chlorine.
- 9 If the charge on an ion is altered might the color be changed? Illustrate by an example.
- 10 Vinegar or lemon juice is used in making salads. Why could not an equivalent amount of hydrochloric acid be used?
- 11 Salt is cheaper and more effective than alcohol for antifreeze mixtures. Why not use it in the radiator?
- 12 What important difference between calcium chloride and carbon tetrachloride is not shown by the formulas  $\text{CaCl}_2$  and  $\text{CCl}_4$ ?
- 13 The sodium ion and the helium atom are alike in what respect?
- 14 The statement was made that crystals contain ions. Why, then, must most crystals of salts be melted before much current will go through them?
- 15 Write an ionic equation showing the reaction of hydrochloric acid upon sodium carbonate to produce water and the volatile gas carbon dioxide.
- 16 Write an ionic equation between sodium phosphate and calcium chloride to show the formation of insoluble calcium phosphate.

### II VOCABULARY TESTING OF NEW TERMS

anode	gram molecular weight	nonpolar compound
cathode	ion	electroplating
electrode	valence electron	strength of acids and
electrolysis	polar compound	bases
electrolyte	electrovalence	covalence
nonelectrolyte	reversible reaction	covalent
electrocardiograph	shared electron	mole

### III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Some Processes Dependent upon Ions
- 2 Stains, and How to Remove Them
- 3 The Electrolytic Production of Sodium Hydroxide from Salt

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 666, 670

## ACIDS

## CHAPTER OUTLINE

## I GENERAL FACTS CONCERNING ACIDS

- (a) Classification
- (b) Properties of acids
- (c) Individual differences
- (d) Antidotes for acids
- (e) Naming of inorganic acids

## II SOME INORGANIC ACIDS

- (a) Hydrochloric acid
- (b) Hypochlorous acid
- (c) Nitric acid
- (d) Sulfuric acid
- (e) Sulfurous acid
- (f) Boric acid

## III SOME ORGANIC ACIDS

- (a) Acetic acid
- (b) Benzoic acid
- (c) Tartaric acid
- (d) Citric acid
- (e) Lactic acid
- (f) Oxalic acid
- (g) Salicylic acid
- (h) Formic acid
- (i) Amino acids
- (j) Palmitic acid stearic acid oleic acid

## IV COMPARISON OF INORGANIC AND ORGANIC ACIDS

## I. GENERAL FACTS CONCERNING ACIDS

There are thousands of inorganic compounds, the majority of which belong to one of three classes, known as acids, bases, and salts. Acids are especially important to the nurse because of their functions in the human body and the place that they hold in the composition of our foods. Fruits and fruit juices contain organic acids. Acids are constantly being formed in the body—gastric juice and urine are distinctly acid solutions.

## Classification

Acids are classified as *inorganic* and *organic*. Organic acids are usually derived from organic matter, i. e., plant or animal matter, while the inorganic commercial acids are derived from inanimate sources. Some of the important acids of each class are listed as follows.

<i>Inorganic</i>		<i>Organic</i>	
Hydrochloric acid	HCl	Acetic acid	H C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
Nitric acid	HNO <sub>3</sub>	Benzoic acid	H C <sub>7</sub> H <sub>5</sub> O <sub>2</sub>
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	Carbonic acid	H <sub>2</sub> CO <sub>3</sub>
Hypochlorous acid	HCIO	Citric acid	H <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O <sub>7</sub>
Sulfurous acid	H <sub>2</sub> SO <sub>3</sub>	Formic acid	H CHO <sub>2</sub>
Boric acid	H <sub>3</sub> BO <sub>3</sub>	Lactic acid	H C <sub>3</sub> H <sub>5</sub> O <sub>3</sub>
Phosphoric	H <sub>3</sub> PO <sub>4</sub>	Malic acid	H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>
Nitrous	HNO <sub>2</sub>	Oxalic acid	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
Hydrosulfuric	H <sub>2</sub> S	Salicylic acid	H C <sub>7</sub> H <sub>5</sub> O <sub>3</sub>
Phosphorous	H <sub>3</sub> PO <sub>3</sub>	Tartaric acid	H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>



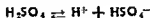
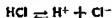
## Properties of Acids, i. e., $H^+$ ions

Ordinarily, we think of an acid as a liquid, but usually these liquids are solutions of gases, liquids, or solids in water. For example hydrochloric acid is a solution of a gas, hydrogen chloride, sulfuric acid is a solution of a liquid, hydrogen sulfate, while boric acid is a solution of a solid.

The formulas show that all acids contain the common element hydrogen, combined with atoms of a nonmetal, or groups of non-metallic atoms called acid radicals. In hydrochloric acid ( $HCl$ ), for example, the nonmetallic element is chlorine ( $Cl$ ), while in sulfuric acid, the acid radical is the sulfate radical ( $SO_4$ ). The non-metals, then, are to be considered as acid forming elements. Since every acid is a hydrogen compound which in aqueous solution produces the  $H^+$  ion, it is reasonable to think of the common and characteristic properties of all acids as being due to the  $H^+$  ion. As has been stated some acids are stronger than others, strength being determined by the concentration of  $H^+$  ions. Use of the terms *concentration* and *strength* should not be confused. A concentrated acetic acid solution contains a high percentage of undissociated acid molecules, thus a concentrated solution of acetic acid is not nearly as strong as a solution of hydrochloric acid, since *strength depends upon degree of ionization*.

The characteristic properties of acids follow

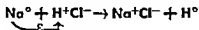
1 ACIDS ARE ELECTROLYTES. All acid solutions will conduct an electric current, that is, the solutions are *electrolytes*. Examples of the ionization of acids in solution follow



2 ACIDS HAVE A SOUR TASTE. When acids dissolve in water they impart a sour taste to the water. Sour tasting solutions generally contain acids. For example, the sour taste in lemons, grapefruit, oranges, and quinces is due to citric acid.

3 ACIDS ACT ON SOME COLORED COMPOUNDS. Many compounds known as indicators change color in the presence of acids. The most common substance so used is blue litmus dye, which changes to a red color in the presence of acid solutions. This is the simplest recognition test for an acid.

4. **ACIDS ACT ON MOST METALS.** When certain *active* metals, as iron, magnesium, or zinc, are put into acid solutions the *metals react* and *hydrogen gas is usually liberated*. From the electron standpoint, metals have atoms that lose one or more electrons to hydrogen ions, which then become ordinary hydrogen atoms.



Then two hydrogen atoms, each sharing its electron with the other, combine to form a molecule of hydrogen gas ( $\text{H}_2$ ) which escapes. The formation of hydrogen may easily be shown by placing a piece of zinc in a test tube which contains a few ml. of dilute sulfuric acid. The presence of the hydrogen is shown by holding a lighted match over the mouth of the test tube. A small explosion usually occurs, when there is some oxygen mixed with the hydrogen. This is a common laboratory test for molecular hydrogen. Pure hydrogen issuing from a jet burns quietly, with a blue flame.



### DISPLACEMENT SERIES

(Partial list)

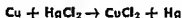
Displace hydrogen from water	{ K
Vigorous reaction with acids	{ Na
	{ Ca
	{ Mg
Displace hydrogen from steam and from acids	{ Al
	{ Zn
	{ Cr
	{ Fe
Displace hydrogen slowly from acids	{ Ni
	{ Sn
	{ Pb
	{ H
Do not displace free hydrogen from acids May react with acids	{ Cu
	{ Sb
	{ Hg
	{ Ag
	{ Pt
	{ Au

Fig 1.

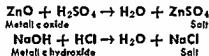
However, not all metals have the ability to displace hydrogen from acids. In Figure 1 metals are arranged in a series showing the order of their activity in this respect. The most active elements

are placed at the top, and they readily displace hydrogen from water. Any metal on the scale above hydrogen will replace hydrogen from an acid, with the exception of concentrated nitric acid which oxidizes the hydrogen to water. The metals below hydrogen on the scale will not displace hydrogen from the acids.

This property of certain metals to displace hydrogen in acids explains why metal utensils are not used in preparing acid foods. It is interesting to note that each metal on the scale will displace any one below it from its salts in solution. For example

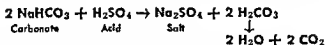


**5 ACIDS ACT ON METALLIC OXIDES AND HYDROXIDES** When water solutions of acids are brought in contact with the oxides or hydroxides of the metals (p. 159), salts and water are formed

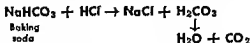


These equations represent *neutralization* (explanation, p. 173), a useful reaction in counteracting the action of an acid or a base.

**6 ACIDS ACT ON CARBONATES** Whenever an acid solution is brought in contact with a carbonate, there is formed a salt and a weak unstable acid, carbonic acid, which quickly decomposes (effervesces) into carbon dioxide and water \*



This is the type of reaction which takes place in a commonly used fire extinguisher as was explained in Chapter III. It is also the reaction which takes place when sodium hydrogen carbonate (baking soda) is used to overcome high acidity of the stomach. Normally the acid in the stomach is either hydrochloric acid or the acids formed by fermentation of foods. The equation shows the action between baking soda and hydrochloric acid



\* Generally speaking salts of any volatile acid react with a nonvolatile acid

The use of baking soda with sour milk (lactic acid) in baking is another example of an acid reacting with a carbonate. It is a similar reaction that takes place when baking soda and orange juice (citric acid) are used with castor oil for laxative purposes. The carbonic acid makes the oil easier to take. Again, the interaction of an acid and a carbonate is the typical reaction of baking powders, since all such powders contain a carbonate and some acid forming substance.

**7. ACIDS ACT ON THE TISSUES.** The physiological action of strong, concentrated acids (as sulfuric, nitric, and hydrochloric) upon the tissues is to destroy the tissues by their corrosive (coagulation and dissolving) action. However, when these acids are in a very dilute form they only abstract water from the tissues. In fevers certain acids may be used to diminish thirst, because they stimulate the flow of saliva. It is for this reason that lemonade (citric acid) finds use in relieving thirst.

Since animal fibers such as silk and wool, like body tissues, are of protein composition, fabrics made of these fibers are also affected by strong concentrated acids. The action is less marked on vegetable fibers (cellulose) such as cotton.

These seven general properties of acids are to be remembered

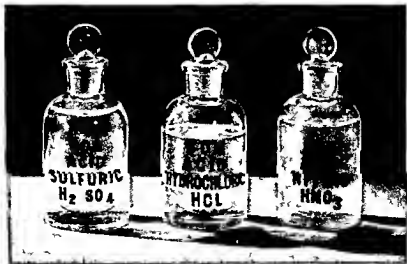


Fig 2—Three Important Mineral Acids. These three common liquid acids are widely used in the laboratory and are indispensable for commercial use. Can you name some other acids used in the hospital?

since they can be applied to almost every soluble acid. The study of each acid, then, will only involve learning the special or "trick" performance of that acid.

### Individual Differences of Acids

Even though acids form a group and exhibit many general properties in common, still they, like people, may possess properties peculiar to themselves. Thus, some acids are very stable (sulfuric), other ones are unstable (carbonic), some are colored (picric), other ones are colorless (tartaric), some are very poisonous (oxalic), other ones are harmless (carbonic) and some may even be used medicinally (citric). A few are not even sour tasting (insoluble atearic), and of course, there is considerable variation in their chemical behavior.

As has been mentioned, all acids in water produce the hydrogen ion,  $H^+$ , and so acids may be defined as *compounds producing hydrogen ions, and no other positive ions, in aqueous solution*. However, it must be remembered that not all hydrogen compounds are acids. For example, sugar ( $C_{12}H_{22}O_{11}$ ) although containing hydrogen does not produce the  $H^+$  ion and therefore is not an acid.

### Antidotes for Acids

From a study of the properties of acids it is evident that any *carbonate*, such as baking soda and chalk, or any mild *hydroxide* as limewater and milk of magnesia, or even soap acids may be used as effective antidotes for mineral acid poisoning. In the case of some *organic acids* special reagents are preferred to the above-mentioned compounds.

To counteract the action of an acid spilled upon the clothing or skin, the first step is to remove as much of it as possible by running water. The remaining acid is then neutralized, preferably by dilute ammonium hydroxide, since any excess of this reagent soon evaporates without injury to the clothing or skin. Acids spilled on the floor may be neutralized by continued additions of baking soda until effervescence ceases.

### Naming of Inorganic Acids

Some acids contain only one other element in addition to hydrogen. These acids are called *binary acids*. *Binary acids* are given names consisting of the prefix *hydro*, to represent the hydrogen, the root of the second element, plus the suffix *ic*. For example,  $HCl$  is

named hydro-chlor-ic acid. Oxygen is the third element in a great majority of the acids. Such acids which contain three elements are called *ternary acids*, and receive their name from the element other than the hydrogen and oxygen. For example,  $\text{HNO}_3$  is nitric acid, and  $\text{H}_3\text{PO}_4$  is phosphoric acid. If three elements unite in different proportions to make several different acids, the best known is given the suffix *ic*, as  $\text{H}_2\text{SO}_4$ , which is called sulfuric acid. An acid with less oxygen than the most common one has the ending *ous*, as  $\text{H}_2\text{SO}_3$  which is named sulfurous acid. It sometimes happens that there are more than two ternary acids composed of the same three elements. In such a case use is made of the prefix *per*, meaning "more," and *hypo*, meaning "less," atoms of oxygen in the molecule. The following ternary acids of chlorine and phosphorus illustrate very well the method of naming them:

#### *Ternary Acids*

$\text{HClO}_4$	<i>per-chlor ic</i>	$\text{H}_3\text{PO}_4$	phosphor <i>ic</i>
$\text{HClO}_3$	chlor <i>ic</i>	$\text{H}_3\text{PO}_3$	.. phosphor- <i>ous</i>
$\text{HClO}_2$	chlor- <i>ous</i>	$\text{H}_3\text{PO}_2$	<i>hypo</i> -phosphor- <i>ous</i>
$\text{HClO}$	<i>hypo</i> -chlor- <i>ous</i>		

In organic chemistry there are so many acids composed of only hydrogen, carbon, and oxygen that it is impossible to use this system for naming organic acids. For this reason many organic acids are named either because of their source (citric acid, from citrus fruits), or some individual characteristic. Also, there are scientific nomenclatures for organic acids.

#### SELF-TESTING QUESTIONS

1. Into what two groups are acids classified?
2. What two fluids of the body are normally acid?
3. The properties of a soluble acid involve the study of what ion?
4. What class of elements is acid forming?
5. Soluble acids are characterized by what general properties?
6. Define an acid.
7. Antidotes for acids depend upon what properties of acids?
8. What are binary acids and ternary acids, and how are they named?

## II. SOME INORGANIC ACIDS

Of the many acids, the following are of special interest to nurses:

### Hydrochloric Acid (HCl):

This acid plays a very important part in the chemistry of the body. Hydrochloric acid is found in the gastric juice where the

acid is present to the extent of about 0.2 to 0.5 per cent. Gastric digestion does not take place except in the presence of this acid, which is produced in the body from salt and water that is taken with the food. In addition to aiding digestion, hydrochloric acid destroys fermenting bacteria which might cause disturbances in the intestinal tract. Sometimes it is necessary to make a gastric analysis in order to find out how much acid is present. If the percentage of  $H^+$  ions is above normal (stomach inflammation or gastritis) the condition is known as *hyperacidity*, but if below normal (gastric juice of many old people) it is called *hypoacidity*. In hyperacidity it is frequently necessary to give some harmless basic acting substance as magnesium oxide, while in hypoacidity very dilute hydrochloric acid supplies this deficiency.

### Hypochlorous Acid ( $HClO$ )

This is a powerful bleaching agent. Its bleaching properties are due to the ease with which it frees its oxygen, and it is the free oxygen which oxidizes the colored materials into colorless compounds.



The oxygen set free in such a manner is called *nascent oxygen* and is much more active than ordinary oxygen gas. Many diseases are caused and communicated by minute microorganisms called bacteria which are readily killed by this acid. In addition to its remarkable antiseptic powers hypochlorous acid dissolves and removes dead tissue.

Calcium hypochlorite, often incorrectly called "chloride of lime," a substance which generates this acid, has long been used as a bleach and disinfectant for sanitary purposes in the home and hospital. Within recent years a sodium compound of this acid called *sodium hypochlorite* has been used in very dilute solution as an antiseptic agent in surgery. The best known solution for this purpose is *Dakin's solution* which is used in washing wounds. Dakin's solution is a neutral sodium hypochlorite solution, containing 0.45 to 0.50 per cent  $NaClO$ . It possesses high toxicity for bacteria and low toxicity for tissue cells. It should be used within 24 hours as upon standing there are formed higher oxides of chlorine and free chlorine which irritate the wound. When the solution is used the patient is so postured that a stream of the solution continually passes into and out of the wound. The sodium hypo

chlorite, like hypochlorous acid, decomposes to liberate oxygen for oxidizing purposes.



Dakin's solution is made by passing chlorine gas into a weak sodium carbonate solution. Care must be taken so that the solution will not be too alkaline because it then has an irritating effect, and the added undesirable action of more readily dissolving blood clots. Commercial preparations containing sodium hypochlorite, Clorox for example, are used for bleaching purposes.

One part of hypochlorous acid in a million parts of water will destroy all the bacteria in water. This method has been adopted by many cities for purifying drinking water. The method usually followed is to pass a stream of chlorine gas from steel cylinders into the water supply. The chlorine with the water forms the hypochlorous acid, which in the presence of the bacterial and organic matter liberates *nascent* oxygen, thus oxidizing and destroying the bacteria.

### Nitric Acid ( $\text{HNO}_3$ ):

Commercially this acid is used for the preparation of such organic compounds as explosives and dyes. When nitric acid is brought in contact with the skin or a piece of wool a yellow stain is produced. Nitric acid is used as a *coagulant* in testing for albumin in the urine (p. 392).

### Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ):

This is the most important commercial acid, and it is used in enormous quantities. In dilute solutions sulfuric acid is used in storage batteries, and in cleaning the surfaces of many metals.



Fig.—3 A Dehydrating Agent. Sulfuric acid not only will absorb free water, but also will withdraw the elements of water from certain organic compounds such as sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). Why can it not be used to dry all gases?



Iron so treated and coated with zinc is called galvanized iron. Enormous quantities of the acid are used in refining petroleum in making fertilizers, and in the preparation of dyestuffs and explosives. Concentrated sulfuric acid has a great affinity for water and for this reason it may be used as a *dehydrating agent*. In this respect, sulfuric acid is so powerful that it will abstract the elements of water from many organic compounds which contain hydrogen and oxygen, leaving carbon as a black residue (Fig. 3). This acid is rarely used in medicine.

### Sulfurous Acid ( $\text{H}_2\text{SO}_3$ ):

This is the result of burning sulfur to form sulfur dioxide and passing the gas into water



Sulfurous acid readily combines with oxygen, taking it from the air or from some unstable substance containing oxygen



On account of this property sulfurous acid is a powerful *reducing agent*. Because of its reducing action, sulfurous acid has strong *bleaching properties* and is used to bleach paper, straw goods, silk, wool, and even such foods as dried fruits, canned corn, and cherries. The bleaching effect is not permanent and disappears after a time, hence materials, like straw hats and paper, become "yellow with age."

### Boric Acid ( $\text{H}_3\text{BO}_3$ ):

This is also called *boracic acid*. It is but sparingly soluble in water and ionizes so slightly in water that it scarcely reddens litmus or exhibits any acid properties. It is a mild *antiseptic* for inflamed mucous membranes of the eyes, nose, or mouth, being especially valuable in a saturated aqueous solution as an eye and mouth wash.

### SELF-TESTING QUESTIONS

9. Where is hydrochloric acid found in the body? In what concentration?
10. How does chlorine react with water?
11. What is Dakin's solution and how do you account for its antiseptic properties?
12. What is the most important commercial acid?
13. Why does fumigating with burning sulfur tend to bleach materials?
14. What saturated acid solution is commonly used for inflamed mucous membranes?

### III. SOME ORGANIC ACIDS

#### Acetic Acid ( $C_2H_4O_2$ , generally written as $H \cdot C_2H_3O_2$ ):

This acid may be derived from alcohol through fermentation brought about by a minute organism present in the so called *mother of vinegar*, or it may be obtained by the destructive distillation of wood. Vinegar may also be made from beer (malt vinegar), from wine (white wine vinegar), or from molasses. Since bacteria are present in the air and on the skins of fruits, acetic acid is produced whenever a dilute solution of alcohol, with some food for the micro organisms, is left exposed to the air. If the percentage of alcohol runs too high (10 per cent), the bacteria are not capable of forming the acid. Acetic acid, as in vinegar, is used as a condiment. *Glacial acetic acid* (99.5 per cent) forms ice like crystals when cooled below  $16^\circ$  centigrade.

#### Benzoic Acid ( $H \cdot C_7H_5O_2$ )

A salt of this acid, sodium benzoate, is used as an antiseptic in the intestinal and urinary tracts, and also as a preservative. Saccharin, a substance approximately 400 to 500 times sweeter than sugar, is a derivative of benzoic acid. Saccharin has no food value as it is not oxidized by the body.

#### Tartaric Acid ( $H_2 \cdot C_4H_4O_6$ )

This acid is found in grapes and many other fruits, however, it usually occurs as potassium acid tartrate ( $KHC_4H_4O_6$ ), a substance which is commonly known as cream of tartar and is useful in making baking powder and effervescent powders as "Seidlitz powders." Tartaric acid is also used in some soft drinks, such as ginger ale. This acid may be used medicinally to increase the flow of urine (diuretic), or as a mild laxative.

#### Citric Acid ( $H_3 \cdot C_6H_5O_7$ )

This acid occurs in many fruits, as oranges, lemons, and berries of all sorts. Citrate of magnesium is used in medicine as a purgative. The juices of fruits containing citric acid, especially oranges and lemons, are used as dietary preventives against scurvy, to replace lost alkali in the blood (explanation p 185), and in the form of hot lemonade to act as a diuretic.

**Lactic Acid ( $H \cdot C_3H_5O_3$ ):**

Milk sours when the sugar present is acted upon by certain microorganisms in the air, producing lactic acid. As mentioned in Chapters I and III, exercise of the muscles produces lactic acid, which is immediately oxidized. However, if undue exercise causes an excessive amount of lactic acid to collect, the oxidation is not completed and fatigue results. Any increase in acidity of the body cells slows down their activity because of the fact that oxidation becomes slower. Then the tissues, being of a colloidal nature, adsorb water and swell. Buttermilk and sauerkraut, which contain lactic acid, will prevent the growth of putrefactive bacteria in the large intestines and so change the intestinal flora. Lactic acid milk finds some use in infant feeding since it produces an easily digested curd, and also is of aid in overcoming diarrhea.

**Oxalic Acid ( $H_2 \cdot C_2O_4$ ):**

This acid occurs in many plants in the form of salts. It is used to remove ink and iron rust from cloth, to clean such metals as copper, and to bleach or clean straw hats. Oxalic acid is very poisonous.

**Salicylic Acid ( $H \cdot C_7H_5O_3$ ):**

In the form of a salt, salicylic acid is used as a food preservative and in medicine as an antiseptic. Oil of wintergreen for treatment of acute articular rheumatism and aspirin for relieving colds and neuralgic pains are products made from this acid.

**Formic Acid ( $H \cdot CHO_2$ )**

Formic acid occurs in nettles and it is secreted by ants. The irritation caused by the sting of an ant or bee is due to the presence of this acid, making understandable why soda is applied to such irritations.

**Amino Acids:**

They are formed both in plants and animals. In animal bodies they are the result of the *digestion* of proteins, and are discussed in the chapter on proteins.

**Palmitic Acid, Stearic Acid, Oleic Acid.**

These three acids are very important since they enter into the composition of many of the fats and oils which occur in our foods. Further discussion will be given in the chapter on fats.

## SELF-TESTING QUESTIONS

15. What acid occurs in vinegar, and for what is it used?
16. What two acids form salts that are used as food preservatives?
17. Where does tartaric acid occur and for what is it used?
18. Citric acid in the form of lemon or orange juice has what use?
19. What organic acid has bleaching properties?
20. Digestion of proteins produces what acids?

## IV. COMPARISON OF INORGANIC AND ORGANIC ACIDS

The effects of certain organic acids such as acetic, tartaric and citric in the body are similar to those of inorganic acids except that they are milder and after absorption act as alkalies. The following table compares their internal action:

<i>Inorganic Acids</i>	<i>Organic Acids</i>
Increase the flow of saliva	Increase the flow of saliva
Aid digestion in the stomach, since pepsin acts only in an acid medium	Aid digestion in the stomach by stimulating the appetite and the flow of gastric juice
Increase the flow of pancreatic juice	Slightly laxative, e.g., lemon juice before breakfast
Increase the acidity of the blood	Increase the flow of urine Act as an alkali in the blood

Organic acids are oxidized in the body cells with the formation of carbonates and consequently are base-forming substances, as will be explained in the chapter on salts (p. 188).

## SELF-TESTING QUESTIONS

21. What are the internal uses of organic acids?
22. How do they differ from inorganic acids in their internal action?

## SUGGESTED ACTIVITIES

## I. THOUGHT-PROVOKING QUESTIONS:

1. Name the three most common strong acids used in the laboratory.
2. How does a strong acid differ from a weak acid?
3. Why should surgical instruments not come in contact with acids?
4. Why should baking powders, or effervescing powders, be kept in a dry place?
5. Give the classification and name of the following compounds:  
 (1)  $\text{H}_3\text{PO}_3$                       (2)  $\text{H}_3\text{PO}_4$

- 6 Why not use a dilute rather than a concentrated or a saturated solution of boric acid as an eyewash?
- 7 Instead of using sour milk and baking soda for baking, what solid acid compound could be used?
- 8 Explain the formation of vinegar from sweet cider
- 9 What are organic acids and how do you account for such a great difference in the chemical action of organic acids as compared to inorganic acids?
- 10 Give the formulas and names of all the possible acids containing the elements hydrogen, sulfur, and oxygen
- 11 In comparing the activity of acids in solution how much replaceable hydrogen must be in each solution?
- 12 What is the underlying general reaction involved when effervescent salts are dissolved in water?

## II VOCABULARY TESTING NEW TERMS

acid	'per'	nascent
binary acid	'hypo'	reducing agent
ternary acid	hyperacidity	

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Antidotes for Common Acids
- 2 Gastric Acidity as a Diagnostic Tool
- 3 Theories Concerning the Formation of the Hydrochloric Acid in the Stomach
- 4 Uses of Hypochlorous Acid and Its Various Salts

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 674, 676

## BASES

## CHAPTER OUTLINE

- |   |  |
|---|--|
| <p><b>I PROPERTIES AND ACTION OF BASES</b></p> <p>(a) Properties of soluble bases</p> <p>(b) Antidotes for bases</p> <p>(c) Strong vs concentrated bases</p> <p><b>II TYPICAL BASES</b></p> <p>(a) Sodium hydroxide or caustic soda</p> <p>(b) Calcium hydroxide or slaked lime</p> | <p>(c) Ammonium hydroxide or aqua ammonia</p> <p>(d) Magnesium hydroxide or milk of magnesia</p> <p><b>III HYDROGEN ION CONCENTRATION</b></p> <p>(a) Hydrogen ion scale</p> <p>(b) Meaning of pH scale</p> <p>(c) Indicators</p> <p>(d) Testing for pH values</p> <p>(e) Hydrogen content vs hydrogen ion concentration</p> <p>(f) Applications of pH value to disease</p> |
|---|--|

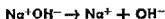
## I. PROPERTIES AND ACTION OF BASES

Properties of Soluble Bases (OH<sup>-</sup> ions):

A study of aqueous solutions of the following typical bases shows that they all have common and characteristic properties

Sodium hydroxide	NaOH	(Caustic soda)
Potassium hydroxide	KOH	(Caustic potash)
Ammonium hydroxide	NH <sub>4</sub> OH	(Ammonia water)
Calcium hydroxide	Ca(OH) <sub>2</sub>	(Lime water)
Magnesium hydroxide	Mg(OH) <sub>2</sub>	(Milk of magnesia)

A glance at the preceding formulas for the common bases shows that they all contain one or more groups of oxygen and hydrogen in combination. This characteristic OH group is called the hydroxyl radical and it is combined with a metal or with the metal like NH<sub>4</sub> radical to form the bases. The metals are base forming elements. Since every soluble base contains the hydroxyl group, which in aqueous solution furnishes the OH<sup>-</sup> ion, it is reasonable to conclude that the characteristic properties of all soluble bases are due to the hydroxyl ion. *A base is a compound which furnishes hydroxyl ions (OH<sup>-</sup>) in solution,*



Soluble bases, therefore, are typical electrolytes. Later, when studying organic compounds, we shall learn about some compounds such as the alcohols and sugars which have one or more

hydroxyl groups, but which are not bases in the sense that they do not ionize to furnish the hydroxyl ion (p. 284). The characteristic properties of bases follow:

1. **BASES HAVE A SOAPY FEELING.** A strong base like sodium hydroxide (lye) when dissolved in water feels slippery or soapy. Such bases are caustic, and can change the natural oil of the skin into soap, and "burn" the skin. On the other hand, calcium

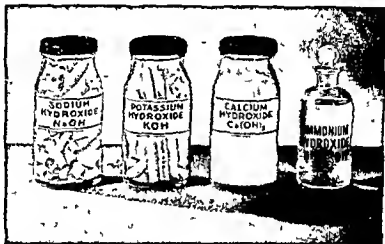


Fig 1—Four important Laboratory Bases. These common laboratory bases have made possible many of the advantages of modern life. What are some of these advantages?

hydroxide (lime water) and dilute ammonium hydroxide (ammonia water) have little corrosive action and can be applied with safety to the skin.

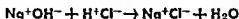
2. **BASES HAVE AN ACRID TASTE.** The biting, metallic taste of a base is decidedly in contrast to the sour taste of an acid. The bitter taste in many toothpastes and in soapsuds is due to the alkali present.

3. **BASES TURN RED LITMUS BLUE.** Bases reverse the color change produced by acids in indicators,\* e. g., they turn red litmus paper blue and turn colorless phenolphthalein solution pink to red. This litmus test is the quickest and simplest test for a base. Other indicators, of which there are many, act similarly, e. g., methyl

\* Indicators are substances which show a decided color in the presence of soluble acids or soluble bases. An indicator, then, is a substance used to show the presence of an acid or a base in solution.

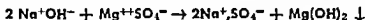
orange becomes red in the presence of  $H^+$  ions, and yellow in the presence of  $OH^-$  ions

4 **BASES REACT WITH ACIDS** When bases react with acids, the hydroxide ion ( $OH^-$ ) of the base combines with the hydrogen ion ( $H^+$ ) of the acid to form an undissociated molecule of water, while the metal ion of the base unites with the negative ion of the acid to form a compound called a *salt*. For example



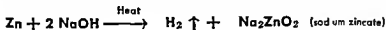
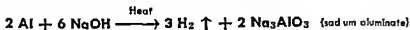
Thus is an example of a reaction called *neutralization*, which will be discussed in the next chapter on salts

5 **BASES REACT WITH SALTS** Frequently a base will react with a soluble salt to form an insoluble base and a salt, e. g.,



6 **BASES ACT ON TISSUES** Bases dissolve proteins and react with fats to form a class of compounds known as soaps. Strong bases, i. e., alkalis, destroy tissues by *dissolving their albumin, reacting with the fats and extracting water*. Bacteria are destroyed in the same manner. The alkalis, therefore, are strong irritants and corrosive poisons. This property of dissolving and decomposing albumin and fats makes basic acting substances very useful as cleansing agents, of which ammonia, lye, and washing soda are common examples. It must be understood that like acids, bases cannot be used to clean all kinds of substances. For example, bases quickly dissolve protein material, such as wool or silk cloth. For this reason it is unwise to use strong laundry soaps in washing silks or woolen material. The free base not only causes a partial destruction of woolen fabrics, but also causes such garments to shrink.

7 **BASES REACT WITH CERTAIN METALS** Some bases, especially sodium hydroxide, react with certain metals such as aluminum and zinc to liberate hydrogen and form salts



It is because of this action that strong alkalis like lye ( $NaOH$ ) or washing soda ( $Na_2CO_3$ ) should not be used in cleaning house



bold utensils made of aluminum or coated with zinc (galvanized iron)

### Antidotes for Bases

It frequently happens that it is useful to know the antidotes for bases. To neutralize bases taken internally dilute acids, such as those present in citrus juices, vinegar, and sour milk, are used.

As in the case of acids, when bases are spilled upon clothing or skin, an attempt should first be made to remove the base by washing in running water, before attempting to neutralize it with any dilute acid.

### Strong vs. Concentrated Bases

Since basic properties are due to hydroxyl ions, the bases which produce a high concentration of  $\text{OH}^-$  ions are strong, that is, strong bases are more highly ionized than weak bases.

The term *concentrated* applied to a base relates to the quantity of dissolved base (solute) in the total solution. When the ratio of solute to solvent is high the solution is concentrated; when this ratio is low the solution is dilute. To illustrate, concentrated ammonium hydroxide solution contains a large amount of dissolved ammonia, it is, however, a weak base because there is a low concentration of hydroxyl ions present. Weak bases, like strong ones, are completely neutralized by acids. The removal of  $\text{OH}^-$  ions by neutralization allows more of the undissociated molecules to ionize until finally all of the base has been acted upon.

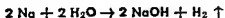
### SELF-TESTING QUESTIONS

1. What is a base? an alkali?
2. What is a test for the hydroxyl ion?
3. Name six characteristic properties of all soluble bases.
4. What is neutralization?
5. In what three ways may a base act upon the tissues?
6. How is it possible to counteract the action of a base taken internally?
7. What is the distinction between strong and concentrated bases?

## II TYPICAL BASES

### Sodium Hydroxide or Caustic Soda ( $\text{NaOH}$ )

When sodium reacts with water, one-half of the hydrogen is liberated as a gas.



Now if the solution is evaporated to dryness, a white compound called sodium hydroxide is left. This compound readily absorbs water, and so quickly disintegrates most vegetable and animal material that it is frequently called "caustic soda." It is sold as a household article under the name of lye, and is valuable for cleaning purposes because it reacts with grease to make a soluble substance, soap (p 361).

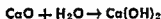
Commercial sodium hydroxide is obtained by electrolysis of a solution of sodium chloride (see p 129)



It is used in the manufacture of hard soaps, potassium hydroxide being used to make soft soaps. Sodium hydroxide is also used extensively in the manufacture of chemicals, rayon and other textiles, paper, and refining of petroleum.

### Calcium Hydroxide or Slaked Lime ( $\text{Ca}(\text{OH})_2$ )

This compound is made by adding water to lime, the process being called slaking



The white compound thus formed is sparingly soluble in water and therefore gives a very low concentration of hydroxyl ions. A clear saturated solution of the calcium hydroxide in water, called *lime water*, is used in medicine to overcome high acidity of the stomach. It is frequently added to cow's milk in order to lessen its acidity, thereby assisting in digestion by preventing too rapid curdling which results in the formation of large tough curds. Lime water is also used in the diet for building bones and teeth, as an antidote in acid poisoning (especially oxalic acid), and in the laboratory as a test for carbon dioxide, since it forms a white precipitate of calcium carbonate with the gas. A suspension of the hydroxide in water is called "milk of lime" and is extensively used as a whitewash. When so used, the calcium hydroxide gradually absorbs carbon dioxide to form insoluble calcium carbonate.

Calcium hydroxide is a moderately active base and is inexpensive to make, but its slight solubility in water prevents its use for many purposes. It is used commercially for removing hair from hides in the preparation of plaster and mortar, and as a white wash.

## Ammonium Hydroxide or Aquo Ammonia ( $\text{NH}_4\text{OH}$ )

Ammonium hydroxide has slightly active basic properties. When heated it quickly decomposes into ammonia and water



Large quantities of ammonia gas are used in the manufacture of ice. For this purpose the ammonia gas is compressed to a liquid which flows through an expansion valve into long series of coils immersed in a brine solution. Metal vessels filled with pure water, are lowered into the brine solution. The liquid ammonia upon expanding absorbs heat from the brine and lowers the temperature of the brine below  $0^\circ\text{C}$ . The brine does not freeze but the pure water in the metal vessels is frozen into cakes of ice after a period of many hours.

If a room which serves as a refrigerator is to be kept cool, the pipes are simply run around the interior walls of the room. These cold storage plants have a temperature low enough to prevent decay and putrefaction.

In the home, ammonia dissolved in water, and known as ammonia water (aqua ammonia) or ammonium hydroxide, is used in preference to other alkalis as a cleanser because any excess of the ammonia left after it is used volatilizes and produces no harm to the goods.

Ammonium hydroxide, being volatile, is more penetrating but less caustic than the other alkalis. Ammonia gas ( $\text{NH}_3$ ) stimulates both respiration and circulation. Medicinally ammonium hydroxide is used as a heart and respiratory stimulant, in liniments to relieve rheumatic pains, and as an antacid.

## Magnesium Hydroxide or Milk of Magnesia ( $\text{Mg}(\text{OH})_2$ )

This slightly soluble compound is a medicinal base much used as a laxative. It is also used in tooth pastes and mouth washes, and to counteract too much acid in the stomach.

### SELF-TESTING QUESTIONS

- 8 What properties does lye have which make it a valuable article for use in the home?
- 9 What is the chief use of sodium hydroxide?
- 10 What is meant by the slaking of lime?
- 11 How is limewater made and for what is it used?
- 12 What is whitewash and why does it form a satisfactory covering for basement walls?

13. What are the commercial and medicinal uses of aqua ammonia?
14. How is magnesium hydroxide used medicinally?

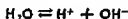
### III. HYDROGEN ION CONCENTRATION

#### Hydrogen Ion Scale:

In the chapter on ionization it is stated that *strength refers to the degree of ionization*, whether applied to an acid or a base. In the case of an acid, the strength of its solution depends upon the concentration of hydrogen ions ( $H^+$ ); and in the case of a base, the strength depends upon the concentration of hydroxyl ions ( $OH^-$ ).

When the number of  $H^+$  ions exceeds that of the  $OH^-$  ions the solution is acid, and conversely, if there is an excess of  $OH^-$  ions, the solution is alkaline. However, when the number of  $H^+$  ions exactly equals the number of  $OH^-$  ions the solution is neutral. Thus pure water is neutral for it is dissociated into equal numbers of  $H^+$  ions (1.008 Gm. in 10,000,000 or  $10^7$  liters of water), and  $OH^-$  ions (17.008 Gm. in 10,000,000 or  $10^7$  liters of water).

The fact that purified water conducts electricity implies the following probable reaction:



the heavy arrow indicating that most of the water exists as electrical neutral particles, i.e., molecules.

Since some fluids of the body are acid, such as the gastric juice and urine, while some are alkaline, as the intestinal fluids and the blood, it is evident that any variation of acidity or alkalinity from the normal condition may be an important factor in the diagnosis of disease. To designate accurately this degree of acidity or alkalinity, that is, to express quantitatively the concentration of hydrogen ions, there has been used in recent years what has been termed the "Hydrogen Ion Scale," the symbol for which is pH.

#### Meaning of pH Scale:

It is no more necessary to know the mathematical derivation of "pH"\* in order to use it, than it is to know the derivation of the term "degree Fahrenheit" when using a thermometer.

\* The logarithm of the number of liters of a solution which contains 1.008 Gm. of hydrogen ions is called the pH value. Since it takes 10,000,000 liters of water to produce 1.008 Gm. of  $H^+$  ions, and the logarithm of 10,000,000 is 7, the pH value of neutral water is 7. This number 7 then is the pH value for all neutral solutions. For a more comprehensive treatise, refer to *The A B C of Hydrogen Ion Control*, LaMotte Chemical Products Co., Baltimore, Md., or any standard textbook of general chemistry.

**Indicators:**

Litmus paper has already been mentioned as useful for indicating when a solution is acid or alkline, but we know nothing therefrom about the exact degree of acidity or alkalinity. All that can be depended upon is that a deep blue or red indicates a higher degree of alkalinity or acidity than do the lighter colors. The substitution of definite *pH* values does away with the indefinite terms "strong" and "weak."

There are numerous dyes or "indicators" which change their colors under the influence of certain concentrations of  $H^+$  ions and  $OH^-$  ions. Litmus solution, for example, shows pink color changes in an acid solution from *pH* 4.6 to *pH* 7.0, the neutral point, and then shows blue color changes in an alkaline solution up to *pH* 8.4. Phenolphthalein, another common indicator, shows pink to red color changes in alkaline solutions of *pH* numbers greater than 8.7. The wide range of these two indicators and their indistinct color changes makes them very inaccurate for determining the exact degree of acidity or alkalinity; consequently, one needs a series of indicators with short distinct color ranges to cover the entire *pH* scale. Fortunately, there are indicators which change colors at other degrees of hydrogen ion concentration, and by their use it is possible to determine accurately the acidity or alkalinity of solutions within a certain short range.

Of the large number of indicators available, those in the table below are chosen as representative ones with short ranges.

**SOME ACID-BASE INDICATORS**

Indicator	<i>pH</i> Range	Color	
		at Lower <i>pH</i>	at Higher <i>pH</i>
Methyl violet	0.1–3.2	Yellow	Violet
Thymol blue	1.3–2.8	Red	Blue
Bromphenol blue	3.0–4.6	Yellow	Blue
Methyl orange	3.1–4.4	Red	Yellow
Methyl red	4.4–8.2	Red	Yellow
Litmus	4.7–8.2	Red	Blue
Bromcresol purple	5.2–8.8	Yellow	Purple
Bromthymol blue	6.0–7.6	Yellow	Blue
Phenolphthalein	8.0–9.8	Colorless	Red
Thymolphthalein	9.3–10.5	Colorless	Blue
Alizarin yellow	10.1–12.1	Yellow	Red

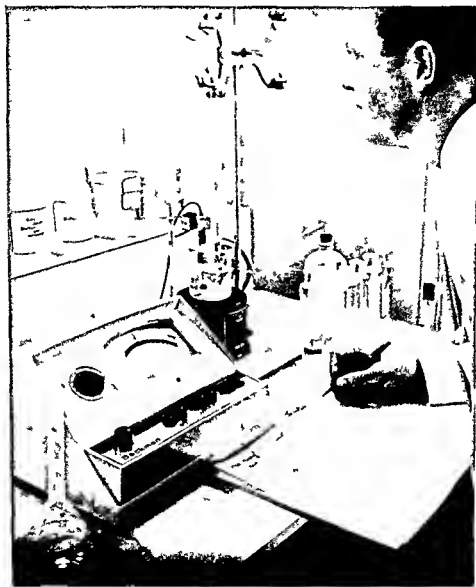


Fig 3—A pH Meter Here a pH meter is being used to show the hydrogen ion concentration in a solution. What does the reading on the meter indicate? Courtesy Beckman Instruments Inc

### Testing for pH Values:

(1) **COLORIMETRIC** In order to determine the pH value of an unknown solution it is first necessary to select experimentally an

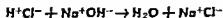
indicator which is sensitive, that is, shows color changes at the pH of the unknown. The table on page 166 lists indicators suitable for this purpose. It is advisable to start with bromthymol blue since this indicator undergoes color changes over the neutral point (see table). In testing a drop of the indicator is added to a small portion of the unknown, a new portion of unknown must be used for each indicator.

For example, if it is found in the preliminary testing that thymol blue is suitable, add one or two drops of this indicator solution to a sample of the unknown. The volume of unknown used, and the container should be the same as employed in the standards. Match this test sample with a set of permanent color standards made up by use of the same indicator in solutions which differ in pH in steps of 2 over the range of the indicator.

(2) **ELECTROMETRIC** The electrometric method makes possible a more rapid and more accurate determination of the pH of a solution. Also, if the solution or fluid to be tested is cloudy (turbid) or colored the colorimetric method obviously cannot be used. The two electrodes of the pH meter are dipped into the solution being examined, and the pH of the solution is then read directly from the dial of the meter (Fig. 3).

### Hydrogen Content vs. Hydrogen Ion Concentration

In neutralizing an acid with a base, *all* of the hydrogen in the acid reacts with a base.



Such determinations are spoken of as the *total hydrogen content* of the acid (un-ionized acid molecules + acid ions), which is quite different from the active hydrogen ion concentration or pH value. Total acidity (and alkalinity in biological materials) of a solution may be compared to the total wealth of a person whereas active acidity considers only the *readily available currency*.

To illustrate. Two acids like sulfuric and boric acids in equivalent concentration have the same *total* hydrogen content, but the boric acid is much weaker than the sulfuric acid, since in solution the boric acid gives only a low percentage of active  $\text{H}^+$  ions. The pH or hydrogen ion scale measures the actual concentration of  $\text{H}^+$  ions, and not the total hydrogen content, consequently, the pH

value is a true measure of the strength of an acid or an alkali. However, active acidity is not always of prime importance. For example, if only enough soda (sodium bicarbonate) is added to sour milk (lactic acid), as a leavening agent in the making of soda biscuits to neutralize the active acid, the biscuits would still have a sour taste. This condition can be corrected by adding sufficient soda to react with the total hydrogen content of the acid.

The following table shows the approximate pH values of some common 0.1N solutions of acids and of basic compounds.

<i>Acid</i>	<i>pH Value</i>	<i>Basic</i>	<i>pH Value</i>
Hydrochloric	1.0	Sodium hydrogen carbonate	8.4
Sulfuric	1.2	Sodium tetraborate (borax)	9.2
Acetic	2.9	Ammonium hydroxide	11.1
Carbonic	3.8	Sodium carbonate	11.6
Boric	5.2	Sodium hydroxide	13.2

### Applications of pH Value to Disease:

There are many valuable applications of the pH control, especially in pathology and bacteriology. The normal pH values of the blood are between 7.3 and 7.5 and, since life becomes endangered if the values are outside the range of 7.0 to 7.8, determination of the hydrogen ion concentration is of great importance to the physician in assisting him to diagnose and treat many diseases such as diabetes, nephritis, and tetany.

### THE pH VALUES OF SOME FLUIDS AND SOLUTIONS

<i>Substance</i>	<i>pH</i>
Hydrochloric acid (0.1 N)	1.0
Gastric fluid	1.5 - 2.8
Vinegar	3.0
Grapefruit juice	3.2
Urine	5.0 - 7.5
Milk	6.6 - 6.9
Saliva	6.8 - 7.2
Water (pure)	7.0
Blood	7.35 - 7.45
Intestinal fluid	7.2 - 8.0
Pancreatic fluid	7.5 - 8.0



Normal gastric juice, which contains some free hydrochloric acid, is approximately one million times as acid as the blood. Here also any great deviation of pH values has a pathological significance. For instance, in pernicious anemia and in cancer of the stomach little acid may be present in the gastric juice, while in indigestion, inflammation and ulcers of the stomach, the pH numbers run low, *i.e.*, the acidity is above normal. Also, it is a well recognized fact that in abnormal variations of acid (outside of pH 1.3 to 4.0) the enzymes of the stomach are inhibited in the digestion of proteins.

In the next chapter it will be learned that pH values of fluids can be maintained reasonably constant by the presence of *buffers*. The most important buffers in body fluids are bicarbonates and phosphates.

It is clearly evident from this brief discussion that disturbances of the hydrogen ion concentration of any fluids in the body are an indication of some pathological disturbance.

### SELF-TESTING QUESTIONS

- 15 What is the hydrogen ion scale used for?
- 16 What is meant by pH values?
- 17 What does pH 7.0 mean?
- 18 When does a pH reading indicate acidity?
- 19 In what way do pH values indicate strong and weak acids or bases?
- 20 Name two common indicators and their color in both acid and alkaline solutions.
- 21 How would you proceed to make a test for pH values?
- 22 How does hydrogen content differ from hydrogen ion concentration?
- 23 Give a pathological application of pH significance.
- 24 Given the pH of a solution, how is the pOH determined?
- 25 Measuring the hydrogen ion concentration of a solution by the colorimetric system depends upon what principle?

### SUGGESTED ACTIVITIES

#### I. THOUGHT PROVOKING QUESTIONS

- 1 Why is lye sold in tin containers? Why would not aluminum containers be practicable?
- 2 Sodium stearate  $\text{NaC}_{17}\text{H}_{35}\text{O}_2$  is a soap. How would this solution react to litmus? Explain.
- 3 Account for the fact that calcium hydroxide when dry has no effect upon red litmus paper.
- 4 To counteract or neutralize acid spilled on clothing, why is ammonium hydroxide used in preference to sodium hydroxide?
- 5 Explain why borax solution shows an alkaline reaction to litmus paper.
- 6 Solution A has a pH of 3.0 and solution B has a pH of 6.0. What is the relationship between their actual hydrogen ion concentrations?

- 7 What is the pH value when the hydrogen ion concentration is 0.0001 gram ions per liter?
- 8 What is the pH of an acid which has one hundred times the acidity of water?
- 9 To counteract the action of large quantities of acid spilled on the laboratory floor or table, why is sodium hydrogen carbonate generally used instead of ammonium hydroxide?
- 10 Using the adverbs faintly, weakly, and strongly, interpret the condition of acidity or alkalinity of the following solutions pH 7.5, 1.3, 13, 5.2, 2.9, 8.4
- 11 In many pathological conditions the hydrogen ion concentration of the urine is increased. Is the pH value raised or lowered?

## II. VOCABULARY TESTING OF NEW TERMS

base	neutralization	indicator
alkali	hydrolysis	pH scale

## III. TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Antidotes for Alkali Poisoning
- 2 Indicators and pH Measurements
- 3 Acid and Alkali in Health and Disease
- 4 The pH of Body Fluids and Tissues

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 679, 681, 684

## CHAPTER IX

# SALTS

### CHAPTER OUTLINE

- |   |                                     |
|---|-------------------------------------|
| I PREPARATION AND PROPERTIES                | (b) Sodium hydrogen carbonate       |
| (a) Neutralization                          |                                     |
| (b) Preparation of salts                    | IV BUFFERS IN THE BLOOD             |
| (c) Incompatibility of some salts           | (a) Buffer action in the blood      |
| (d) Properties of salts                     |                                     |
| (e) Ionization of salts                     | V SALTS IN THE HUMAN BODY           |
| (f) Typical salts                           | (a) Formation of salts              |
|   | (b) Chemical balance of the body    |
| II TYPES AND NAMES OF SALTS                 | (c) Importance of salts in the body |
| (a) Normal, acid, and basic salts           | (d) Effects of salts on the cells   |
| (b) Naming of salts                         |                                     |
| III HYDROLYSIS OF SALTS                     | VI ALKALOID SALTS                   |
| (a) Why some salt solutions are not neutral | (a) Properties of alkaloids         |
|   | (b) Antidotes                       |

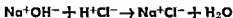


Fig 1—Household Salts Can you name one or more medical uses for any of these salts? Courtesy, Raymond Fearon, Philadelphia

### I. PREPARATION AND PROPERTIES

#### Neutralization:

When solutions of an acid and a base are brought together in the proper proportions, the characteristic properties of both are lost, *e. g.*, there is no effect of the mixture upon either blue or red litmus paper. *From this fact we infer that the hydrogen ions of the acid and the hydroxyl ions of the base must have been removed from the solution.* An examination of the following equation



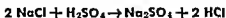
shows that the negative hydroxyl ion of the base has combined

with the positive hydrogen ion of the acid to form undissociated water, while the remaining part of the base ( $\text{Na}^+$ ) has combined with the remaining part of the acid ( $\text{Cl}^-$ ) to form one of the class of compounds which we call *salts*. Such a reaction between an acid and a base with the formation of a salt and water is known as *neutralization*. Upon evaporating the solution the concentration increases and the sodium and chloride ions begin to join together, and the solid salt crystallizes out of solution, once the saturation point is exceeded.

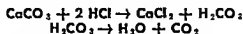


Fig 2—An American Salt Mine. Common salt is obtained from mines or by evaporation of water. For what purposes is salt needed by the body? Courtesy, International Salt Company, Inc

Since there are many acids and base-forming substances in nature, and since acids and bases are very active chemically, salts are constantly formed in the crust of the earth. These salts are also undergoing a decomposition to form new compounds. It is also true that from one salt may be formed an acid, which in turn may react with another salt to form still different compounds. Thus common salt upon treatment with sulfuric acid will produce hydrochloric acid:

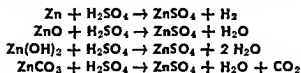


The hydrochloric acid then may decompose another salt to form still another acid and another salt, as shown by the following equations



### Preparation of Salts

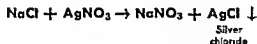
From the preceding paragraph it is evident that a salt may be formed by the union of an acid and a base or by the action between certain acids and various salts. A soluble salt may also be formed by the action of an acid upon a metal, its oxide, hydroxide, or its carbonate as illustrated in the following equations



These reactions you may recall as typical of acids (p 145). *A salt, then, is a combination of a metal, or the metallic radical  $\text{NH}_4$ , with a nonmetal or nonmetallic radical of an acid, as Cl, Br,  $\text{SO}_4$ ,  $\text{NO}_3$ , and  $\text{PO}_4$ .*

### Incompatibility of Some Salts:

Salts may also be formed by several other methods, one of which is worthy of mention, namely the reaction between two soluble salts. Salts formed in this way are often insoluble, e g, in the following equation silver chloride is an insoluble salt



As a therapeutic measure a solution of the salt silver nitrate is often used in bladder infections. Soon, however, the germicidal action of the silver nitrate is stopped, as the sodium chloride in the urine reacts with the silver nitrate to form insoluble silver chloride. Again, as a prophylaxis against gonorrheal infection, most states require that a drop of 1 to 2 per cent solution of silver nitrate be placed in the eyes of newborn babies. In this instance, the salty tears, or the use of a physiological saline solution, stops the further action of the silver nitrate on the tissue cells of the eyes. As another example, potassium iodide forms an insoluble salt when used

internally as a treatment for lead poisoning. As two salts may react to form new salts with different properties you can understand why it is seldom a good idea to administer two salts at the same time. The properties of the new salts might do more harm than good.

From these statements it is evident that a nurse should be aware of the fact that many salts, and other compounds, for that matter, are incompatible. The incompatibility of a number of pairs of compounds follows.

#### SOME COMMON INCOMPATIBLES

---

Magnesium sulfate	and	Ferric chloride
Sodium bicarbonate	and	Ammonium chloride
Sodium bicarbonate	and	Ferric chloride
Sodium bicarbonate	and	Limewater
Sodium bromide	and	Ferric chloride
Sodium chloride	and	Silver nitrate
Calcium chloride	and	Ephedrine
Ferrous iodide syrup	and	Quinine or codeine
Magnesium sulfate	and	Quinine
Potassium iodide	and	Strychnine sulfate
Sodium bicarbonate	and	Ephedrine hydrochloride
Sodium salicylate	and	Caffeine citrate

---

#### Properties of Salts

In studying acids and bases we study respectively the hydrogen ion ( $H^+$ ) and the hydroxyl ion ( $OH^-$ ), but in examining the formulas of such salts as silver nitrate ( $AgNO_3$ ), mercuric chloride ( $HgCl_2$ ), or magnesium sulfate ( $MgSO_4$ ), we see that *there is no ion that is common to all salts*. For this reason we are unable to list a number of properties common to all salts as we did in the case of acids and bases. For instance some salts taste sour, some alkaline, others salty or metallic, and a few even taste sweet. We also may find that salts vary in their action toward indicators, some being acid, some alkaline, and some neutral. It is even true that a few salts are *oxidizing agents* (chlorates, nitrates, permanganates) while others combine with oxygen and with sulfites and therefore are *reducing agents*. Nevertheless we do find similarities in such physical properties as color, taste, and solubility. Especially is this true between certain salts of the same metal ( $NaCl$ ,  $Na_2SO_4$ ,  $NaNO_3$ ) or between various salts of the same acid ( $NaCl$ ,  $KCl$ ,  $NH_4Cl$ ).

The chemical reactions of some salts with other salts (p 175), with water (hydrolysis) to form acids and bases (pp 182, 183), with acids (p 175), and with bases (p 175) have already been stated. Reactions of salts with metals to form another salt and another metal have been mentioned (p 146) and the discussion of salt and metal contacts that are to be avoided in laboratory, hospital, and household practice is presented later on under the subject of metals (p 215).

### Ionization of Salts:

As has been stated (p 133), most salts are strong electrolytes, that is, they are highly ionized. As a consequence, reactions between salt ions usually are rapid. Some salts though, like mercuric chloride, only slightly ionize and consequently react slowly in solution. The degree of ionization in the case of electrolytes represents the ratio of *free* ions to the un-ionized molecules, or to associated ions. Notice in the following table that the percentage of ionization in a N/10 solution of most salts ranges from 65 to 85 per cent.

<i>Types of Salts</i>	<i>Percentage of Ionization in a N/10 Solution</i>
$M^{+1} A^{-1}$ (e.g., NaCl)	83 to 86
$M^{+2} A_2^{-1}$ (e.g., $BaCl_2$ )	72 to 77
$M_2^{+1} A^{-2}$ (e.g., $Na_2SO_4$ )	70 to 73
$M^{+2} A^{-2}$ (e.g., $ZnSO_4$ )	50 to less

### Typical Salts:

Of the many hundreds of salts, several that are widely used in industries are common salt (NaCl), washing soda ( $Na_2CO_3 \cdot 10 H_2O$ ), limestone ( $CaCO_3$ ), and Chile saltpeter ( $NaNO_3$ ). However, there are many other important salts, some of which are used quite extensively in medicine (Fig. 3). The following salts of the four common acids HCl,  $H_2SO_4$ ,  $HNO_3$  and  $H_2CO_3$  are so frequently used in medicine that a brief discussion of them is given on the next page.

Since there are so many salts, space does not permit us to make an individual study of them or even to mention all of the important ones, however, a detailed study of medicinal salts is given in *Pharmacology*.

## MEDICINAL SALTS OF SOME COMMON ACIDS

<i>Salt</i>	<i>Common Name</i>	<i>Use</i>
Sodium chloride ( $\text{NaCl}$ )	Tablet salt	Saline solution
Mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ )	Calomel	Purgative
Mercuric chloride ( $\text{HgCl}_2$ )	Corrosive sublimate	Antiseptic and antisyphilitic
Magnesium sulfate ( $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ )	Epsom salts	Purgative    Allays inflammation
Barium sulfate ( $\text{BaSO}_4$ )	"Barium"	Coats the stomach and intestines with a compound, opaque to the x ray
Calcium sulfate ( $\text{CaSO}_4$ ) <sub>2</sub> · $\text{H}_2\text{O}$	Plaster of Paris	Casts for broken bones
Potassium nitrate ( $\text{KNO}_3$ )	Saltpeter	Diuretic
Silver nitrate ( $\text{AgNO}_3$ )	Lunar caustic	Antiseptic caustic, astringent
Bismuth subnitrate ( $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ )	"Bismuth"	Anti-irritant of the bowels, astringent
Ammonium carbonate [( $\text{NH}_4$ ) <sub>2</sub> $\text{CO}_3 \cdot \text{H}_2\text{O}$ ]	Precipitated chalk	Stimulant in syncope, expectorant in bronchitis
Bismuth subcarbonate ( $\text{Bi}_2\text{O}_3\text{CO}_3$ )		Antacid, in roentgenography
Calcium carbonate ( $\text{CaCO}_3$ )		Antacid, detergent, protective in gastric ulcer
Ferrous carbonate ( $\text{FeCO}_3$ )		In anemia (in the form of Bland's pills)
Magnesium carbonate ( $\text{MgCO}_3$ )		Antacid, in hyperacidity, dusting powder, cosmetic
Sodium bicarbonate ( $\text{NaHCO}_3$ )	Baking soda	In hyperacidity, in acidosis, alkaline wash
Sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ )	Washing soda	Preparation of alkaline baths





Fig 3—X ray Therapy Machine This 2 000 000 volt x ray machine makes possible a scientific treatment of deep seated malignancy For what disease would this unit find its widest use? Courtesy, General Electric Company

### SELF-TESTING QUESTIONS

- 1 What is always formed in neutralization?
- 2 What are five general methods of preparing salts?
- 3 What might be the danger of administering different salts at the same time?

4 Why do not salts have common properties?

5 State the chemical name the common name and a medicinal use of three important chlorides sulfates nitrates and carbonates

## II. TYPES AND NAMES OF SALTS

### Normal, Acid, and Basic Salts:

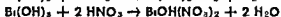
If an acid has more than one replaceable hydrogen atom\* per molecule it is possible to make two salts, depending upon the amounts of base used. The following examples illustrate this

acid salt formation  $\text{NaOH} + \text{H}_2\text{CO}_3 \rightarrow \text{NaHCO}_3 + \text{H}_2\text{O}$

normal salt formation  $2 \text{NaOH} + \text{H}_2\text{CO}_3 \rightarrow \text{Na}_2\text{CO}_3 + 2 \text{H}_2\text{O}$

The one salt ( $\text{NaHCO}_3$ ) still retains one atom of hydrogen, since there are not enough hydroxyl ions to unite with all of the hydrogen. In forming the second salt ( $\text{Na}_2\text{CO}_3$ ) all of the hydrogen of the acid is displaced by the metal sodium. The former salt is known as an *acid salt* and is called *sodium hydrogen carbonate* (baking soda), while the latter ( $\text{Na}_2\text{CO}_3$ ) is a *normal salt* and is called *sodium carbonate* (washing soda).

Similarly there are produced hydroxy or more commonly called *basic salts*, when only part of the hydroxyl ions of a base are replaced by a nonmetal or a nonmetallic radical as for example



When a hydroxy salt as basic bismuth nitrate ( $\text{Bi(OH)}_2\text{NO}_3$ ) is dried, it loses a molecule of water to form bismuth subnitrate or oxynitrate,  $\text{BiONO}_2$ , a white insoluble compound, called an *oxy salt*. Bismuth subnitrate acts upon the mucous membranes of the stomach and intestines much like a face powder does upon the skin, and as a consequence is used to coat, protect, and heal ulcers of the intestinal tract. Moreover, this salt is also used like barium sulfate in making x ray pictures of the digestive tract. Bismuth subnitrate can act as an alkali to neutralize the acid of the stomach and in this way is said to "sweeten" an acid stomach.

The use of the terms *acid*, *basic*, and *normal* in classifying salts is to point out the composition or structure of each salt, not its

\* Replaceable hydrogen of an acid refers only to the hydrogen capable of forming ions. In the case of organic acids as will be shown later not all of the hydrogen is replaceable.

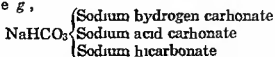
behavior toward an indicator. Thus sodium bicarbonate ( $\text{NaHCO}_3$ ) is *classified* as an acid salt, but in water solution this salt gives an alkaline test with litmus paper. The reason for this is given later in this chapter.

### Naming of Salts:

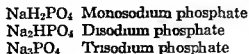
Salts are named from the metal and the acid from which they are derived. A salt of a binary acid, i.e., an acid containing one other element besides hydrogen, is given the name of the two elements composing it, with the ending "ide." Thus  $\text{NaCl}$  is read "sodium chloride." The ending "ate" is used for the names of salts of ternary acids which end in *ic*. If the name of the ternary acid ends in *ous*, the ending of the salt is "ite." Thus  $\text{Na}_2\text{SO}_4$ , a salt of sulfuric acid, is named sodium sulfate, while  $\text{Na}_2\text{SO}_3$ , a salt of sulfurous acid, is named sodium sulfite. If the name of the ternary acid has a prefix, the prefix appears in the name of its salts as shown in the examples below.

Formula	Acid	Formula	Sodium Salt
$\text{HClO}_4$	Per-chlor <i>ic</i>	$\text{NaClO}_4$	Sodium per chlor-ate
$\text{HClO}_3$	Chlor <i>ic</i>	$\text{NaClO}_3$	Sodium chlor ate
$\text{HClO}_2$	Chlor <i>ous</i>	$\text{NaClO}_2$	Sodium chlor ite
$\text{HClO}$	Hypo chlor <i>ous</i>	$\text{NaClO}$	Sodium hypo chlor ite
$\text{HCl}$	Hydrochlor <i>ic</i>	$\text{NaCl}$	Sodium chlor ide

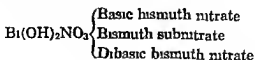
Acid salts are distinguished by the word *hydrogen* or *acid*, or by the prefix *bi*, e.g.,



The use of *bi* (above) is somewhat confusing as in some compounds it means two. Thus  $\text{HgCl}_2$  is frequently called bichloride of mercury. If more than one metallic atom replaces hydrogen, as in a tribasic acid, the following nomenclature should be used:



*Basic salts* usually contain the word *basic* in their names, or less often they contain the prefix *sub*, thus



*Mixed salts* formed by more than one metal replacing hydrogen of acids are named thus



*Double salts* result when two different salts crystallize simultaneously from one solution to give crystals which contain both salts in a definite proportion. The *alums*, such as potash alum,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{ H}_2\text{O}$  are examples

### SELF-TESTING QUESTIONS

- 6 What is a normal salt an acid salt and a basic salt?
- 7 Name and give an important use of a normal acid and basic salt
- 8 How are salts of ternary acids named?
- 9 May an acid salt be alkaline in solution?
- 10 State the names and formulae of the sodium salts of five acids which contain chlorine
- 11 How are acid basic and mixed salts named?
- 12 In what way does the double salt differ from the mixed salt?
- 13 What is the rule for naming salts of binary acids?
- 14 What are some medicinal uses for bismuth subnitrate?

### III HYDROLYSIS OF SALTS

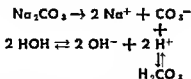
Water has been previously characterized as a nonelectrolyte and nonconductor of electricity, but very careful measurements reveal that the purest of water has a very slight ionic dissociation (0.00000018 per cent) into hydrogen ions and hydroxyl ions. This fact helps to explain why aqueous solutions of certain salts are not neutral.

#### Why Some Salt Solutions Are Not Neutral

If one prepares water solutions of a variety of normal salts it will be found that some show an acid reaction to litmus, others an alkaline reaction, and still others a neutral effect. Since normal salts contain neither hydrogen nor hydroxyl radicals, they cannot in themselves be directly responsible for the acidic and the basic solutions. The fact that some normal salts in water solution are

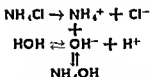
acidic while others are basic is explained in terms of reactions of ions of the salts with water. This type of reaction of a salt, involving water, is called *salt hydrolysis*.

Sodium carbonate is typical of those salts whose water solutions are basic. A solution of this salt consists of sodium ions and carbonate ions. It has been pointed out that water itself is only slightly ionized. The following equations express these facts



The hydrogen ions and carbonate ions combine to a considerable degree to give the weak, molecular carbonic acid. As a result of this, hydrogen ions are withdrawn. Sodium ions and hydroxyl ions show no tendency to combine, recall that sodium hydroxide is a strong base, and in water may be viewed as completely ionic. Hence there will be in the solution a higher concentration of hydroxyl ions than hydrogen ions, and consequently the solution is basic and turns red litmus paper to blue. Notice that the sodium carbonate is a salt which is derived from a strong base (NaOH) and a weak acid ( $\text{H}_2\text{CO}_3$ ).

An opposite effect is obtained with the salt ammonium chloride. In water this salt exists as freely moving ions



Here we notice that hydroxyl ions and ammonium ions combine extensively to form the weak, molecular ammonium hydroxide. This consumes hydroxyl ions. The chloride ions and hydrogen ions do not combine inasmuch as hydrochloric acid is a strong, highly ionized electrolyte. The result is that the concentration of hydrogen ions in the solution is higher than the concentration of the hydroxyl ions, and consequently the solution reacts acidic.

Salts like sodium chloride, which are derived from strong acids and strong bases, do not hydrolyze, hence they form solutions which are neutral. Those salts which are derived from weak acids and weak bases, for example, ammonium carbonate, are extensively



Fig. 5—Alkaline Producing Foods. Some of these foods have an acid taste. Still they are base forming in the blood. To what classes do most alkaline producing foods belong?

### Chemical Balance of the Body:

When foods are burned outside of the body an acid or a basic ash may be obtained. Consequently when oxidized in the body, they may be considered as either acid forming or base forming foods (Figs. 4, 5). In general, the acids of fruits are so oxidized in the body that an alkaline ash results. On the other hand, some foods such as cereals and meat, which do not have an acid taste, yield acidic substances when they are digested.

The blood and the tissues are slightly alkaline, a condition which prevents an accumulation of acids in the body. The kidneys, too, function in removing acids and thereby help maintain the alkalinity of the blood stream (p. 484). The excess of alkali (mostly due to sodium bicarbonate) over the acid in the blood is known as the *alkaline reserve*, and this margin, though very small, is vitally important and is called the "chemical balance."

To keep the individual healthy, efficient, and to maintain his physical endurance, the blood must preserve this margin of alkalinity. As a guide to building up this chemical balance, some of the common foods have been classified on the next page.\*

### Importance of Salts in the Body:

Salts do not furnish heat or energy, yet they are very essential to life. We will learn later that in, general, salts (1) are necessary for protoplasm, tissue, and body structure; (2) maintain the elasticity and irritability of the muscles and nerves; (3) maintain the neutral or slightly acid or alkaline condition of the body fluids and (4) assist in maintaining normal osmotic pressure condition; (p. 532).

\* Chemistry of Foods and Nutrition, Sherman, The Macmillan Co.

**ALKALI-PRODUCING FOODS**

These foods should be used in adequate amounts to maintain the favorable alkaline balance of the body

*Degree of Alkalinity  
per 100 Gm*

Almonds	12 38
Apples	3 76†
Asparagus	0 81
Bananas	5 56†
Beans dried	23 87†
Beans, lima, dried	41 65
Beets	10 86
Cabbage	4 34
Cantaloupe	7 47†
Carrots	10 82
Cauliflower	5 33
Celery	7 78
Chestnuts	7 42
Currants, dried	5 97
Lemons	5 45
Lettuce	7 37
Milk, cow's	2 37
Oranges	5 61
Peaches	5 04
Peas, dried	7 07
Potatoes	7 19†
Radishes	2 87
Raisins	23 68
Turnips	2 68

**ACID-PRODUCING FOODS**

These foods should always be balanced by adequate amounts of alkaline foods

*Degree of Acidity  
per 100 Gm*

Bread, white	7 1
Bread whole wheat	7 3
Corn, sweet, dried	5 95
Crackers	7 81
Cranberries	†
Eggs	11 10
Egg white	5 24
Egg yolk	26 69
Fish haddock	15 07
Fish, pike	11 81
Meat, beef, lean	13 91
Meat chicken	17 01
Meat, frog	10 36
Meat, rabbit	14 80
Meat, veal	18 52
Meat pork, lean	11 87
Oatmeal	12 98
Oysters	30 00
Peanuts	3 9
Prunes, plums	†
Rice	8 1

The following foods have neither chemical reaction

Butter	Cream	Sugar
Starch	Lard	

† These foods have been found experimentally to be very efficient in reducing the body acidity

‡ The ash of these fruits is alkaline but because of substances that form hippuric acid in the body they increase the acidity of the urine

In general all fruits vegetables nuts and milk are alkaline in the body

Of all the sources of mineral salts needed by the body, milk ranks first (p 603) It contains the balanced quantity of all the salts (iron excepted), which are needed for growth of tissues, and strong bones and teeth Of particular importance in milk is the salt, calcium hydrogen phosphate Green leafy vegetables, fruits, eggs, and whole cereal products are also excellent sources of mineral salts

Each salt has an important and special function in the body. The blood, for example, is practically a 1 per cent solution of salt and water containing the corpuscles. Albumin and sugar are also present in the solution.

Iron in the hemoglobin molecule gives color to the blood. The amount of iron in the body is only about 0.004 per cent of the weight of a person, an amount equivalent to a single nail. However, this very small amount of iron is of the greatest importance to life. If the foods do not contain sufficient iron, then the lowered production of hemoglobin may result in anemia, lowered vitality, and insufficient oxidation in the cells.

Sodium chloride is an essential salt in the body, as the hydrochloric acid which is necessary in the gastric juice for digestion is made from it. The presence of salt in the fluids which bathe the tissues assists in maintaining the osmotic equilibrium. It is the salt in the blood which stimulates the action of the heart muscle. A lack of salt slows the heart's action, a condition evidenced by low blood pressure. Since excretion of common salt in sweat is so great, it is a common practice to restore the salt lost by perspiring laborers, or by patients with an unusually high fever (hyperthermia), by giving them salt tablets ( $\text{NaCl}$ ), along with copious amounts of water. In meats sodium chloride is present in sufficient quantities to balance the potassium, calcium, and magnesium salts. Plants, however, do not provide enough sodium chloride, and as a result herbivorous animals seek salt licks in order to maintain the necessary chemical balance. Too much salt in food may interfere with absorption and the utilization of food, while an excessive amount may cause death. In human nutrition, salt is used primarily to make more appetizing a larger variety of foods, especially the vegetables.

Sodium ions determine the amount of water held in the tissues, too high a concentration of sodium ions causing too much water to be retained, a condition known as edema or dropsy. Consequently in cases of water retention (edema) sodium chloride is restricted in the diet, and sodium free salt substitutes ( $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ) are used.

Calcium salts give rigidity and firmness to the bones. A lack of these salts produces poor teeth and rickets in children (see p. 593). Calcium salts are absolutely essential for the clotting of the blood and they are often administered as drugs in certain diseases or



prior to certain operations to assist the clotting properties of blood. It is the calcium salts which partially cause *contraction* of the cardiac muscle, while the sodium and potassium salts cause *relaxation*. The normal beating of the heart requires that the fluid bathing its muscles contain the proper proportion and concentration of calcium, sodium, and potassium ions. Metallic ions furnish the hydroxides which neutralize the acids produced by body activity. It is highly important that the acidity (lactic acid) of a cell does not increase too much, for then its activity is lessened as recognized by the sense of fatigue. Sometimes this overacidity causes a swelling of the tissues, since the colloidal material of the cell adsorbs more water in the presence of an acid. As has been previously stated, in the case of all salts of organic acids, *e g*, citrate of magnesia, the acid radicals are oxidized in the body to carbon dioxide and water, which reactions leave the metallic ions free to act as base-forming substances.

### Effects of Salts on the Cells.

The moment salts enter the alimentary tract they begin to withdraw fluid from the cells by osmosis, sometimes in sufficient quantity to distend the intestines and cause bowel movement. Part of the salts, however, is absorbed and carried by the blood to the cells which are bathed by the lymph. If the percentage of salt in the lymph is greater than in the cells, water is withdrawn from the cells. In case the percentage is less, the cells absorb water from the lymph, a process called "diffusion." Diffusion differs from *osmosis* in that it occurs without the intervention of an animal membrane. It may now be understood how the activity of certain organs such as the kidneys may be increased by certain salts.

Such metallic salts as those of mercury, iron, and arsenic are absorbed and form insoluble compounds with the proteins of the cells. If there is an excessive amount of these salts the cells are irritated, injured, and they show symptoms of poisoning. The functioning of salts in helping to regulate body processes and to make possible normal metabolism is presented on pages 526-531.

### SELF-TESTING QUESTIONS

- 28 In what four ways are salts essential to life?
- 29 What are the functions of the following salts in the body: iron salts, sodium chloride, calcium salts?
- 30 How do certain salts activate the kidneys?

## VI. ALKALOID SALTS

## Properties of Alkaloids.

Certain nitrogenous compounds of both vegetable and animal origin act like alkalis in combining with acids to form salts. These compounds are called alkaloids, meaning *alkali like*. With a single exception, the alkaloids are derived from plants belonging to the dicotyledons, and in some cases the same plants contain several alkaloids. The liquid alkaloids (as pilocarpine, nicotine and conine)

## SOME IMPORTANT ALKALOIDS AND THEIR USES

Name	Source	Uses
Cocaine $C_{17}H_{21}NO_4$	Coca leaves	Local anesthetic but being extremely toxic has been largely replaced by Novocain
Codeine $C_{18}H_{21}NO_2$	Opium	Sedative. Similar but less powerful than morphine
Morphine $C_{17}H_{19}NO_3$	Opium	Sedative narcotic hypnotic. Relieves pain. Used with scopolamine in 'twilight sleep'
Quinine $C_{20}H_{20}N_2O_2$	Cinchona bark	Specific in malaria. Reduces fever. Tonic or bitter to stimulate the appetite
Strychnine $C_{21}H_{22}N_2O_2$	Nux vomica	Stimulates the brain and spinal cord. A heart and respiratory stimulant in colic. Tonic
Nicotine $C_{10}H_{14}N_2$	Tobacco (0.6 to 8.0%)	Stimulates nervous system. Causes weak pulse, nausea and vomiting
Pilocarpine $C_{11}H_{15}N_2O_2$	Pilocarpus	Increases perspiration. Acts like nicotine
Atropine $C_{17}H_{23}NO$	Deadly night shade	Secretory depressant. Dilates the pupil. Used in ophthalmic surgery
Brucine $C_{28}H_{28}N_2O_4$	Nux vomica	Physiologically one twenty-fourth as strong as strychnine
Heroin $C_{21}H_{22}NO_5$	Derivative of morphine	Similar to morphine. Used as sedative and to lessen coughing
Emetine $C_{20}H_{26}N_2O_6$	Ipecac	Treatment of amebic dysentery, and pyorrhea

have a disagreeable odor Both the liquid alkaloids and the white crystalline, solid alkaloids (as quinine, atropine, strychnine, morphine, codeine, and cocaine) have a strong, bitter taste and many are extremely poisonous

Of the large number of vegetable alkaloids, only a very few have been prepared synthetically The first five in the table on page 192 are commonly used in medicine Atropine and cocaine have been largely replaced by artificial alkaloids

Since many of the *alkaloids are insoluble in water*, their soluble salts are commonly used in medicine For example, strychnine reacts with sulfuric acid to form strychnine sulfate, a soluble salt In the same way morphine sulfate and other soluble alkaloidal salts are made Alkaloids may be given hypodermically as well as by mouth, and since their effect occurs chiefly after entering the blood stream it is obvious that only the soluble salts are used

### Antidotes:

Alkaloids are frequently dispensed as drugs in the hospital owing to their very energetic physiological action upon the body Continued use makes some of them habit forming drugs, while an over dose may prove very toxic Since the alkaloids and their salts are precipitated by tannic acid or potassium permanganate and are made incapable of absorption, these and other so called alkaloidal reagents are used as antidotes in alkaloid poisoning cases The alkaloids are not easy to identify, but as a class they may be precipitated by phosphomolybdic and phosphotungstic acids, and in some cases may be identified by color reactions with sulfuric acid and an oxidizing agent

### SELF-TESTING QUESTIONS

- 31 What does alkaloid mean?
- 32 What are three liquid alkaloids?
- 33 State a use of the five most important alkaloids in medicine
- 34 Why are the salts rather than the pure alkaloids used in medicine?
- 35 What two reagents are antidotes for alkaloid poisoning?

### SUGGESTED ACTIVITIES

#### I THOUGHT PROVOKING QUESTIONS

- 1 Neutralization is the reverse of what other type of chemical change?
- 2 What are the most important sources of some of the different salts needed in the body?
- 3 Why is it that carbonic acid and not nitric acid can form acid salts?
- 4 Why is there danger connected with the use of alkaloids?

- 5 Explain why orange juice, or a small dose of sodium hydrogen carbonate, is frequently used in the treatment of colds
- 6 Complete the following equations
 

$\text{HCl} + \text{NaOH}$	$\rightarrow$	_____	+	_____
_____ $\text{HCl} + \text{Ca}(\text{OH})_2$	$\rightarrow$	_____	+	_____
_____ $\text{HCl} + \text{Bi}(\text{OH})_3$	$\rightarrow$	_____	+	_____
$\text{HNO}_3 + \text{KOH}$	$\rightarrow$	_____	+	_____
$\text{H}_2\text{SO}_4 +$ _____ $\text{NH}_4\text{OH}$	$\rightarrow$	_____	+	_____
_____ $\text{H}_2\text{SO}_4 +$ _____ $\text{Bi}(\text{OH})_3$	$\rightarrow$	_____	+	_____
_____ $\text{H}_3\text{PO}_4 +$ _____ $\text{Ca}(\text{OH})_2$	$\rightarrow$	_____	+	_____
- 7 Give the formula of an acid salt of sulfuric acid, and of phosphoric acid ( $\text{H}_3\text{PO}_4$ )
- 8 State the chemical name of the following compounds and classify each as to whether it is an acid, base, normal salt, acid salt, or basic salt
 

(a) $\text{K}_2\text{CO}_3$	(e) $\text{ZnSO}_4$	(i) $\text{KHC}_4\text{H}_4\text{O}_6$ (cream of tartar)
(b) $\text{Cu}(\text{OH})_2$	(f) $\text{Na}_2\text{HPO}_4$	(j) $\text{Na}_2\text{B}_4\text{O}_7$ (borax)
(c) $\text{NH}_4\text{Cl}$	(g) $\text{HClO}_3$	(k) $\text{NaHCO}_3$ (baking soda)
(d) $\text{HNO}_3$	(h) $\text{NH}_4\text{HCO}_3$	(l) $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$ (white lead)
- 9 How does a solution of the acid salt, sodium hydrogen carbonate, react with litmus paper?
- 10 When will an acid salt react as an acid toward litmus paper?
- 11 How do you account for the fact that of the two acid salts disodium acid phosphate,  $\text{Na}_2\text{HPO}_4$ , and monosodium acid phosphate,  $\text{NaH}_2\text{PO}_4$ , one is alkaline acting in the blood and one is acid acting?
- 12 A patient has been taking cold tablets which frequently contain some alkaloid. She feels chilly and drinks a cup of hot tea or coffee. Why shouldn't this be done?
- 13 Two soluble salts react to form two new soluble salts. How may the newly formed salts be separated?
- 14 Of the three sodium phosphates, which is acid which slightly alkaline, and which very alkaline?
- 15 How do you account for the constant pH value of the blood even though the amount of acid received varies considerably?

## II VOCABULARY TESTING OF NEW TERMS

salt	normal salt	"ide"
diffusion	acid salt	"hypo"
alkaloid	basic salt	"ate"
	buffer	"ite"
	alkaline reserve	"hyper"

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Use of Common Salt in the Body
- 2 The Alkaloids
- 3 Incompatibility of Certain Medicinals
- 4 Importance of Minerals in the Diet

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 686, 689

## NONMETALS AND METALS

## CHAPTER OUTLINE

- |  |   |
|--|---|
| <p><b>I NITROGEN AND ITS COMPOUNDS</b></p> <p>(a) Occurrence and properties of nitrogen</p> <p>(b) Nitrogen essential to plant life</p> <p>(c) Uses of nitrogen</p> <p>(d) Compounds of nitrogen</p> | <p><b>IV OXIDES OF CARBON</b></p> <p>(a) Carbon dioxide</p> <p>(b) Carbon dioxide-oxygen cycle</p> <p>(c) Carbon monoxide</p>   |
| <p><b>II HALOGENS, SULFUR, PHOSPHORUS</b></p> <p>(a) The halogens</p> <p>(b) Sulfur</p> <p>(c) Phosphorus</p>  | <p><b>V METALS</b></p> <p>(a) Classifying elements as metals</p> <p>(b) Listing metals according to activity</p> <p>(c) Tarnishing of metals</p> <p>(d) General methods of removing tarnish</p> <p>(e) Cleaning of some common metals</p> |
| <p><b>III. CARBON AND ITS COMPOUNDS</b></p> <p>(a) Natural forms of carbon</p> <p>(b) Chemical properties</p>  | <p><b>VI ALLOYS OF METALS</b></p> <p>(a) Nature of alloys</p> <p>(b) Properties of alloys</p>   |

## I. NITROGEN AND ITS COMPOUNDS

About seventy of the elements are base forming and as such are called *metals*. Calcium, for example, is a base-forming element, since its oxide unites with water to form the base, calcium hydroxide



The remaining elements, with their general properties somewhat the opposite of metals, have acid-forming properties and are called *nonmetals*\*. Sulfur, for example, is an acid forming element since its oxide unites with water to form sulfurous acid



Before taking up the study of some of these elements, in order to have some idea of the general differences between metals and nonmetals, the following comparison is given

\* From the electron standpoint, an element which loses electrons is left positively charged and is called a metal, while any element which gains electrons is called a non metal. Some elements, and especially those having three to five valence electrons may act as metals or as nonmetals. Such elements are said to be *amphoteric*. For instance, their oxides under some conditions may be acidic and under others may be basic.

<i>Metals</i> (Fe, Cu, Hg, Ag, etc.)	<i>Nonmetals</i> (O, N, P, Br, etc.)
Solids (except Hg) Opaque, with mirror like surfaces Malleable, ductile Good conductors of heat Good conductors of electricity Base formers Lose electrons to form $+ ions$	Mostly gases (or brittle solids) Mostly transparent Not very malleable or ductile Poor conductors of heat Poor conductors of electricity Acid formers Gain electrons to form $- ions$

### Occurrence and Properties of Nitrogen:

The inert gas nitrogen makes up about four fifths of the air and is of great importance, since it is indirectly essential to life and is present in all living matter, both animal and vegetable. In the combined state, nitrogen is found in only a few mineral compounds ( $\text{NaNO}_3$ ,  $\text{KNO}_3$ ), and most of these compounds have been produced by plant or animal life. Proteins, which form a valuable constituent of our foods, are nitrogen compounds. In fact, nitrogen is the principal element in the living cell.

Nitrogen, like oxygen and hydrogen, is a colorless, odorless, tasteless gas, but differs in its chemical action in that it is not active at

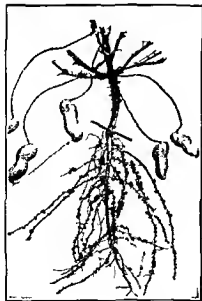


Fig 1—Multiplying Bacteria at Work. Observe the nodules formed by the nitrogen fixing bacteria which convert free nitrogen of the air into soluble nitrates. The pea nuts are used for what purposes? Courtesy, U S Dept of Agriculture

ordinary temperatures At high temperatures, however, nitrogen does combine directly with a few elements to form a class of compounds called *nitrides*

### Nitrogen Essential to Plant Life

Although nitrogen is essential to the life of all cells, yet, with few exceptions, the cells of plants have no power to utilize the free nitrogen of the air It was long known that certain plants, such as clover, peas and beans, would thrive well on ground which would not produce good grain crops Also, it was known that the soil after growing these crops of clover, peas, and beans would become enriched, and would then produce a good crop of grain Years of investigation showed that these plants produced little nodules on their roots, and that in these nodules (Fig 1) lived microorganisms which possessed the power of taking free nitrogen from the air and converting it into compounds of nitrogen for plant food These root nodule bacteria do not necessarily feed their captured nitrogen directly to their hosts, but excrete into the soil considerable quantities of the essential building blocks of the proteins, as aspartic acid which the host-plant is able to use Upon death the plant roots enrich the soil It is for this reason that crops are planted in rotation, i e., about every third year the ground is enriched by planting clover or some similar legu

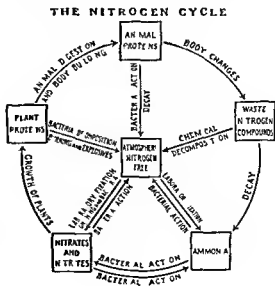


Fig 2—The Nitrogen Cycle  
The processes involving nitrogen in the lives of plants and animals never end hence the term nitrogen cycle

minous crop. Recent investigation has disclosed that higher plants can capture nitrogen directly from the air without the aid of root bacteria.

In addition to the nitrogen-fixing bacteria which change the nitrogen of the air into soluble nitrates, there are the denitrifying bacteria, which are constantly breaking down the nitrogen compounds in the soil. In this way large quantities of nitrogen are returned to the air as shown in Fig. 2.

### Uses of Nitrogen:

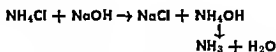
The nitrogen in the air serves to dilute and thereby diminish the chemical activity of the oxygen. Nitrogen enriches the soil through the agency of certain plants, from which the same or other plants build up complex compounds in their growth. Animals feed upon these plants, and assimilate the nitrogenous matter which then becomes an essential part of animal tissue. In both plants and animals the nitrogen is present chiefly in the form of proteins, which are complex compounds containing the elements carbon, hydrogen, oxygen, and nitrogen, and frequently phosphorus and sulfur. It should be remembered that the human body needs nitrogen, but cannot use the nitrogen of the air or any other form of nitrogen unless it be in the form of a protein molecule. The exact structure of this protein molecule is unknown. The simplest formula calculated for oxyhemoglobin,  $C_{723}H_{1118}N_{207}S_2FeO_{210}$ , gives us some idea of the complexity of the protein molecule.

### Compounds of Nitrogen:

While a great many compounds of nitrogen are known it is sufficient to become acquainted with only a few of the simpler ones. Nitric acid ( $HNO_3$ ) has been discussed (p. 151).

**AMMONIA ( $NH_3$ ):** Ammonia gas is produced whenever nitrogenous organic matter as blood, flesh, or manure decays. Originally it was prepared by simply heating the hoofs and horns of animals, and passing the evolved gas into water. Some ammonia is obtained by heating soft coal in the absence of air, a process called destructive distillation. The direct synthesis of ammonia from nitrogen and hydrogen by the Haber process is the most important commercial source. In the laboratory, ammonia is readily prepared by heating any ammonium salt with a strong base as shown in the following equation:





Ammonia is a colorless gas, having a characteristic irritating, and penetrating odor, and it is extremely soluble in water. When dissolved in water it is called aqua ammonia, ammonia water, or ammonium hydroxide, and in this form it has a household use as a cleanser and water softener,



Some soap is generally added to the household ammonia in order to assist in the cleaning. Ammonia, liquefied under pressure is used in refrigeration plants to produce cooling by its own expansion. Manufactured ice is made by this process as explained on page 162.

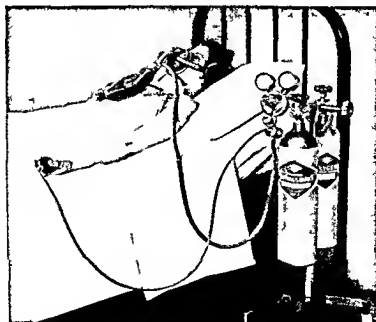


Fig 3—Analgesia Controlled by the Patient. By means of a specially constructed machine for the induction of nitrous oxide and oxygen a patient breathes himself into a state of analgesia. Releasing the pressure on the bulb automatically shuts off the nitrous oxide and at the same time increases the flow of oxygen. Why is there no danger of complete unconsciousness? Courtesy The Ohio Chemical and Mfg. Co.

**SALTS OF AMMONIA** Ammonia combines with any acid, and the compound formed is an ammonium salt, for example



Ammonium chloride is the salt formed in the above reaction. All of the ammonium salts are very soluble and some find extensive use in medicine as heart stimulants and expectorants. Smelling salts are made by mixing unstable ammonium carbonate with some pleasant smelling extract.

**NITROUS OXIDE ( $\text{N}_2\text{O}$ )** Nitrous oxide is the practically odorless, light gas which the dentist and physician use as an anesthetic for many operations (Fig. 3). It was the first gas ever used to render a patient unconscious of pain. When inhaled in limited quantities, nitrous oxide produces a kind of hysteria and consequently has often been referred to as "laughing gas." It is our weakest inhalation anesthetic, but our safest one because oxygen is always the antidote; the color of the patient, the breathing and reflexes are guides showing the depth of anesthesia. When mixed with oxygen (8 to 10 per cent) as an anesthetic it is quick in action, pleasant to take, evanescent in its effect, and because of its nontoxicity causes no permanent effect of any significance. Relaxation of the muscles with nitrous oxide is very slight, and consequently this anesthetic is not used where deep relaxation is required, as in major surgery.

**AMINO ACIDS** These are discussed more fully later (p. 384), and it is, therefore, sufficient to know at this time that these acids are important compounds of nitrogen and are the end products of the digestion of protein. They are absorbed from the intestine, taken into the blood stream and carried to the tissues. Amino acids are the decomposition products of meats, eggs and other proteins by enzymes or by bacterial action.

### SELF-TESTING QUESTIONS

- 1 How would you define a metal and a nonmetal from their properties and also from the electron standpoint?
- 2 How does nitrogen occur in nature?
- 3 What are the chemical properties of nitrogen?
- 4 How does nitrogen of the air enrich the soil?
- 5 How do we obtain the nitrogen that serves to build the tissues of the body?
- 6 What is the composition of the protein molecule?
- 7 How is ammonia produced?

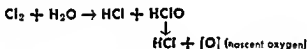
- 8 What are some common names for  $\text{NH}_4\text{OH}$ ?
- 9 For what is ammonium hydroxide used?
- 10 What are the medicinal uses of ammonium salts?
- 11 Why is nitrous oxide considered a good anesthetic?
- 12 How are amino acids formed and what does their presence indicate?

## II. HALOGENS, SULFUR, PHOSPHORUS

### The Halogens

The nonmetallic elements, chlorine (Cl), bromine (Br), iodine (I), and fluorine (F), make up a group of elements called the "halogens," i.e., salt formers. These elements have very similar properties, and all of them are poisonous and corrosive, and combine with hydrogen to form acids.

**CHLORINE** This is a greenish yellow gas with a disagreeable, suffocating odor, and a very irritating action on the mucous membranes of the nose and mouth. Chlorine is very poisonous, and exposure to it for short periods produces serious pulmonary trouble. When chlorine is breathed it combines with the hydrogen of the water in the tissues and forms hydrochloric acid, which destroys the air cells in the lungs.



"Bleaching powder ( $\text{CaOCl}_2$ ), a compound prepared from slaked lime and chlorine, is used as a convenient source of chlorine for whitening paper and bleaching cotton and linen fabrics. As has been stated, liquid chlorine is extensively used in the disinfection of public water supplies (p. 78), and the treatment of sewage.

Even though chlorine has been widely used as an antiseptic, its irritating and poisonous properties have prevented its use in or on the human body. Nevertheless, some inorganic chlorine compounds (hypochlorites) as chlorinated lime, Javelle water, and Dakin's solution (p. 150), have been used. Owing to the instability of these inorganic compounds, however, certain organic chlorine compounds (e.g., the chloramines) have been widely substituted. They keep better and liberate chlorine more slowly under favorable conditions. Chlorine is used to form the hypnotic chloral ( $\text{CCl}_3\text{CHO}$ ), and the anesthetics chloroform ( $\text{CHCl}_3$ ) and ethyl chloride ( $\text{C}_2\text{H}_5\text{Cl}$ ). Considerable chlorine in the form of carbon tetrachloride ( $\text{CCl}_4$ ), and trichloroethylene, is used in the drycleaning busi-

ness. Carbon tetrachloride is used in making fire extinguishers of the Pyrene type

**BROMINE.** This is a dark red liquid which has a strong suffocating smell. It gives off irritating fumes and has an intense corrosive action on the skin, causing a very serious burn; consequently, great care should be used in handling this element. Bromine acts on the nose and throat as does chlorine, and also irritates the eyes. Sodium, potassium, and ammonium bromides are all used medically as sedatives, but their continued use disturbs digestion, and brings on the state of brominism. Other sedatives are discussed on page 298.

**IODINE** This is a dark gray solid which easily vaporizes into violet-colored fumes. It is almost insoluble in water but very soluble



Fig 4—Hyperthyroidism and Hypothyroidism. Overactivity and underactivity of the thyroid gland markedly influence the energy metabolism. In which case will it be above normal? Courtesy, University Hospitals, Cleveland

in alcohol which contains a small quantity of potassium iodide. This solution has very valuable antiseptic properties, and it is sold commercially as tincture of iodine. Because of its coagulating effect upon the tissues, and consequent inability to penetrate or irrigate deep wounds, its use is limited to disinfections of skin and surface wounds. Concentrated solutions and repeated applications of iodine are irritating and destructive to tissues. Many compounds of iodine are used in medicine. Recently, preparations called *iodophors* have been developed for a more effective use of iodine. In minute quantities, iodine is a constituent of most natural waters, and as a constituent of the active principle of the thyroid gland it is essential in maintaining the normal rate of metabolism. A deficiency of iodine in some instances, at least, brings on an enlargement of the thyroid gland known as simple goiter. Small amounts of sodium iodide in table salt have been successfully used where the gland is deficient in its secretion of iodine and has not become enlarged to any great extent. Where there is an overproduction of the active principle, as in exophthalmic goiter, the use of an iodide is to be avoided since it might bring on hyperthyroidism. Patients with goiter are also being treated with radioactive iodine (p. 234.)

When a very small amount of iodine solution is brought in contact with starch a blue color is produced. This characteristic reaction is used as a test for either iodine or starch.

**FLUORINE:** This element is the most reactive of the nonmetals and certain salts find important industrial uses. Of interest is the use of fluorides for drinking water to prevent dental caries. Research has shown that a fluoride content from .5 to 1.2 parts per million is a desirable concentration for this purpose. However, higher concentrations of fluorides in water result in mottled enamel of teeth in children. At the present, many communities are practicing fluoridation of water.

### Sulfur:

We are all familiar with the yellow appearance of the nonmetal, sulfur, and we have previously learned that it is moderately active, burns in air, and unites readily with many other elements. It is used in the preparation of sulfur dioxide, sulfuric acid, carbon disulfide, metallic sulfides, and vulcanized rubber. Medicinally, it finds a use in the treatment of some parasitic skin diseases such as scabies.

## Phosphorus:

Phosphorus, like sulfur, exists in different forms called "allotropic" forms. In the case of phosphorus, the two most common forms are known as *white* and *red phosphorus*. The white variety is very flammable, a violent poison, and quite soluble in carbon disulfide. Red phosphorus is not so active chemically, is not poisonous, or soluble in carbon disulfide. The chief uses of phosphorus are in making matches, rat poison and hard alloys. Phosphates are important in maintaining the fertility of the soil. Compounds of phosphorus exist in the bones, teeth, muscles, nerves, and brain tissues. In the blood, one form of phosphorus is associated with the fat content. In the body, a deficiency of phosphates makes weak bone structure.

### SELF-TESTING QUESTIONS

- 13 What are the halogens?
- 14 Why is chlorine poisonous?
- 15 For what is chlorine used?
- 16 What compounds of chlorine have been used for antiseptic purposes?
- 17 Give a medicinal use of sodium, potassium and ammonium bromides.
- 18 What is tincture of iodine?
- 19 What is the importance of iodine in the thyroid gland?
- 20 What is the effect of too much or too little iodine in the thyroid glands?
- 21 Name a medicinal use of sulfur.
- 22 How do the two forms of phosphorus differ in their properties?
- 23 How is phosphorus important in the body?

## III. CARBON AND ITS COMPOUNDS

Carbon and its compounds have been known and prized from remotest antiquity as they are so important in supplying man's greatest needs—food, warmth, and clothing. Large quantities of carbon are found in the free state in nature, coal, for example, is an impure form of carbon.

### Natural Forms of Carbon:

**COAL** Coal exists in several varieties which represent different stages in the decomposition of vegetable matter in the absence of air. At one time in our earth's history, vegetation flourished to a remarkable extent. This vegetation evidently became covered to a great depth with earth, where under enormous pressure and in the absence of air, it underwent a slow decomposition with the evolution of gases, and the formation of coal.

The many varieties of coal found on the market may be roughly divided into two great classes, namely, *hard* or *anthracite* coal, and *soft* or *bituminous* coal. Bituminous coal contains more volatile matter than the hard coal. It burns with a sooty flame and evolves more gases (hydrocarbon) than hard coal. Soft coal is commonly used as fuel, and in the manufacture of illuminating gas.

Some forms of coal, such as cannel coal and lignite, contain even less uncombined carbon, while peat is a first stage in the formation of coal from plants.

**GRAPHITE** This is a crystalline form of carbon found in nature. Most of the graphite is now made by heating coal in an electric furnace. Graphite is made up of soft, flat scales which present a good sliding surface, and for that reason it finds extensive use as a lubricant. Some graphite is used to make "lead" pencils, and crucibles. It also serves as a paint for iron ware.

**DIAMOND** This is the third form of carbon to be found in nature. It is also crystalline and is colorless when pure. The different colors in diamonds are due to the foreign substances dissolved in the carbon. The diamond is the hardest substance found in nature and consequently has a use in making many cutting instruments. The real value of the diamond lies in its high index of refraction (ability to bend rays of light), which produces a sparkling play of colors. A diamond as found very seldom weighs more than 20 Gm. The largest diamond found weighed  $3025\frac{3}{4}$  carats (a carat is about 0.2 Gm), but subsequent cuttings reduced the largest single portion of this diamond to  $516\frac{1}{2}$  carats.

**AMORPHOUS CARBON** This is a noncrystalline form and is a result of the decomposition of vegetable and animal matter in the presence of heat and in the absence of air. The common physical properties of carbon, as the color and the specific gravity, are the results of the temperature at which the carbon is formed. The blackest form of carbon is made at the lowest temperature.

**LAMP BLACK AND CARBON BLACK** Lamp black is practically pure carbon and is produced by the incomplete combustion of hydrocarbons, compounds of hydrogen and carbon, such as heavy oil. The operation is very analogous to the smoking of a coal oil lamp. The hydrogen of the hydrocarbons burns, but much of the carbon is left unburnt as a soft, greasy powder. Lamp black is used to make paint, and India and printer's ink. Carbon black is made by the same method from natural gas. It is the blackest and most

finely divided substance known to commerce, and is used in the rubber industry to improve the durability of rubber products

**BONE BLACK** This is obtained by heating bones in the absence of air. It is used in the sugar industry to remove the yellow coloring matter from sugar solutions. Bone black is also used to adsorb the color in certain oils. It contains considerable calcium phosphate.

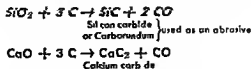
**CHARCOAL** This is made by heating wood without access to air. The volatile matter expelled consists of such valuable substances as wood alcohol, acetic acid, and acetone. The operation is known as *destructive distillation*. The charcoal left is used as a fuel. On account of their remarkable power to adsorb gases, charcoal tablets are used as a gastric medicine. Gas masks used in warfare, and now in many industries as a protection against poisonous gases, contain a specially made charcoal known as activated charcoal. Activated charcoal also finds an important use in the purification of industrial waters (p 79). One volume of such charcoal is able to adsorb several hundred volumes of some gases.

**COKE** This is a harder form of carbon, and is prepared at high temperatures by the destructive distillation of soft coal. The volatile materials here are coal gas, ammonia, carbolic acid, benzene, and tar. Coke is a very valuable fuel.

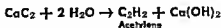
### Chemical Properties

In its combined form, carbon exists in thousands of compounds. Natural gas, petroleum, carbonates, and all living organisms are largely composed of compounds of carbon.

The forms of carbon differ in their physical and to some extent in their chemical properties; however, all forms are odorless, tasteless solids, insoluble in water. At ordinary temperatures carbon is inactive, but at high temperatures it is very active and combines directly with oxygen to form either carbon dioxide ( $\text{CO}_2$ ) or carbon monoxide ( $\text{CO}$ ). Carbon also combines with a few elements to form compounds called *carbides*, e.g.,

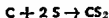


The calcium carbide is used in making acetylene gas





Carbon also unites with sulfur to make carbon disulfide, a good solvent.



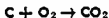
### SELF-TESTING QUESTIONS

24. What is a hydrocarbon?
25. How does anthracite coal differ from bituminous coal?
26. What is graphite and for what is it used?
27. What are two crystalline forms of carbon?
28. How are the amorphous forms of carbon produced?
29. For what is each amorphous form used?
30. With what will carbon unite?
31. Name two important carbides and their chief use.
32. What is destructive distillation?

## IV. OXIDES OF CARBON

### Carbon Dioxide ( $\text{CO}_2$ ):

This is a colorless gas that is always formed when carbon fuels burn completely.



Carbon dioxide is also formed in respiration, and during the fermentation of sugar to make alcohol. Carbon dioxide is given off from volcanoes and is found in coal mines under the name of *choke*



Fig. 5—Pertussis Outfit. Inhalations of carbon dioxide-oxygen keep lungs sufficiently clear so that the paroxysms may be appreciably diminished in frequency and intensity. It is especially useful in cases of whooping cough. How does this mixture of gases promote recovery? Courtesy, Ohio Chemical and Mfg. Co., Cleveland, Ohio.

*damp*. Since it reacts with limewater to make a white precipitate, this property constitutes a simple test for carbon dioxide

In respiration, any increased exertion causes a correspondingly increased amount of carbon dioxide to be given off by the tissues and absorbed by the blood. Since carbon dioxide readily unites with water, forming carbonic acid, the hydrogen ion concentration in the blood is increased.

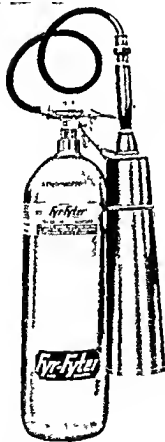


Fig. 6—A  $\text{CO}_2$  Fire Extinguisher. The cylinder is charged with carbon dioxide under pressure. What are advantages of this type of extinguisher? Courtesy of Fyr-Fyter Company

This resultant increased acidity in the blood stimulates the nervous centers of respiration to an increased activity. The respiration is increased in order to expel the carbon dioxide from the blood, thereby lowering the hydrogen ion concentration. Consequently more rapid breathing after exertion is not wholly due to a need for more oxygen.

In the chapter on oxygen we learned that pure oxygen is often administered in cases of suffocation or collapse. Experiments have shown that a mixture of 93 per cent oxygen with 7 per cent carbon dioxide is much better to administer than pure oxygen, since this mixture promotes deeper breathing. Deep breathing enables the patient to expel more quickly a poisonous gas, such as carbon monoxide, and enhances the possibilities for recovery. For prevention of postoperative complications, a common practice is to give the oxygen carbon dioxide mixture by inhalation for three minutes every hour for 24 hours, to patients who have had major operations with prolonged anesthesia.

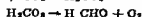
Carbon dioxide is a food for plants, and it is used in the manufacture of soda water and similar beverages. It is a good fire extinguisher, since it is a heavy gas and a nonsupporter of combustion (Fig. 6). It also serves as an aerating agent in baking since it produces the desired lightness. In the solid form, under the name of "Dry Ice," carbon dioxide is used as a commercial refrigerant.

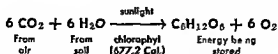
### Carbon Dioxide-Oxygen Cycle:

Carbon is a necessary element for both plant and animal structure. Animals obtain carbon through the agency of the plants, while the plants, in turn, obtain it from the carbon dioxide of the air.

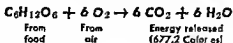
In the presence of sunlight and the catalytic agent, chlorophyll, the plant takes the carbon dioxide from the air, combines it with the water from the ground, and stores it up in the plant as a carbohydrate with the absorption of solar energy. This chemical process is called *photosynthesis*.\*

\* According to theory there is first formed carbonic acid then formaldehyde which latter substance combines with several of its molecules (polymerizes) to form glucose. This process continues with the elimination of water and produces polysaccharides (starch and cellulose). The equations are as follows:





Notice that solar energy (677.2 Cal) is required to produce a gram molecule of a simple carbohydrate (180 Gm) Upon being used as a food, oxidation releases the potential energy (calories stored therein) with a reversal of the above chemical reaction



This, then, shows the interdependence of plants and animals for both carbon dioxide and oxygen (Fig 7) No other chemical reac-

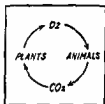


Fig 7—Carbon Dioxide—Oxygen Cycle

tion in all the world is of such great importance to man since through photosynthesis the carbohydrates produced not only supply us with food but they are also used by the plant in the manufacture of fats and proteins Furthermore, only in this manner do we get energy directly or indirectly from plant and animal life

### Carbon Monoxide (CO)

This is always formed when carbon burns in a limited supply of oxygen



The gas burns with a pale blue flame and may be observed by watching the flame over any coal fire Its most striking chemical property is its ability to combine with oxygen Carbon monoxide is extremely poisonous, causing more deaths than all other gases Just as long as fire is used for heat and power, the hazards of carbon monoxide can never be entirely eliminated Air containing 0.1 per cent of carbon monoxide gas will produce insensibility in two hours and death shortly thereafter Carbon monoxide is often formed in mine explosions, and birds have been used to warn the men of the

presence of this gas. Birds breathe a larger volume of air for their weight than does man (higher rate of metabolism) and hence are more quickly overcome.

Today it is a practice to use instruments (meters) to detect and record concentrations of carbon monoxide in the air.

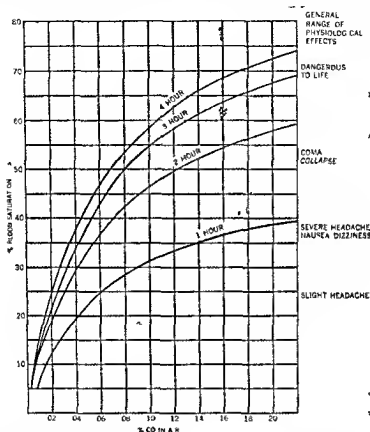


Fig 8—Effects of Carbon Monoxide on Human Beings Courtesy, Mine Safety Appliances Company

When carbon monoxide is breathed it combines with the red corpuscles of the blood to form carbon monoxide hemoglobin (carbonyl hemoglobin), and renders these corpuscles incapable of taking up oxygen, thus producing carbon monoxide intoxication. This, of course, results in suffocation, death being due to paralysis of the respiratory system. In ordinary suffocation the blood is blue, but in the case of carbon monoxide poisoning, the blood is a bright red, almost like arterial blood.

Since incomplete combustion always produces carbon monoxide, great care should be exercised wherever combustion is taking place. The danger is great wherever automobile engines are running in enclosed buildings. Also since all cars average about 5 per cent of carbon monoxide in their exhaust, it is evident that this alone constitutes a great health hazard (Fig. 9). The last statement



Fig 9—Exhaust Fumes Contain a Poison With the motor running, the air in a closed garage soon becomes fatal, because of the accumulation of poisonous carbon monoxide gas. What makes this gas so dangerous?

means that many automobiles produce approximately one cubic foot of carbon monoxide per minute, which by accumulation in a closed one-car garage is sufficient to produce paralysis in 10 or 15 minutes and death within half an hour. When asphyxia does occur it is the result of the failure of respiration. At such times, the poisonous carbon monoxide must be removed, the respiratory stimulant carbon dioxide lost during the development of asphyxia must be restored, and the oxygen-carrying power of the blood must be renewed. Methylene blue (1 per cent) has been claimed as an antidote for carbon monoxide as well as for cyanide poisoning.

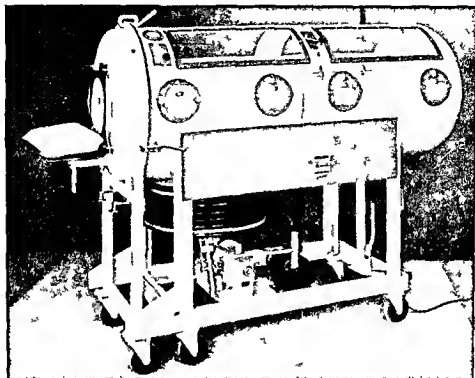


Fig 10—Drinker Collins Respirator Courtesy Warren E Collins Inc

Whether hypodermically injected methylene blue can promote recovery is to be questioned, but it is well established that recovery may be brought about by the inhalation of oxygen which changes the carbon monoxide hemoglobin back to oxyhemoglobin and at the same time saturates the blood with oxygen

In this "machine age" the machine shown in Fig 10 produces artificial respiration when in certain cases normal respiration ceases

Gas masks used for adsorbing carbon monoxide contain a mixture of metallic oxides, mostly  $\text{MnO}_2$ , called "Hopcalite," which acts as catalyzer to make the carbon monoxide combine with the oxygen of the air to form carbon dioxide

### SELF-TESTING QUESTIONS

- 33 In what ways is carbon dioxide formed?
- 34 What is choke damp?
- 35 What is a test for carbon dioxide?
- 36 How does carbon dioxide aid in anesthesia?

- 37 What are some commercial uses of carbon dioxide?
- 38 What is photosynthesis?
- 39 How do plants and animals regulate the amount of oxygen and carbon dioxide in the air?
- 40 How is carbon monoxide produced?
- 41 What is the most important chemical property of carbon monoxide?
- 42 What is the effect of breathing carbon monoxide?
- 43 How may the presence of carbon monoxide be detected?
- 44 What is the immediate treatment for asphyxia when it is caused by carbon monoxide?

## V. METALS

### Classifying Elements as Metals:

So far we have dealt almost exclusively with the nonmetallic elements, such as oxygen, nitrogen, the halogens, sulfur, phosphorus, and carbon. Each of these elements (C excepted) with more than half of the electrons needed to fill out its outer atomic shell usually gains electrons, and consequently has a negative

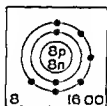


Fig 11—Nonmetal Oxygen (O) Six electrons in outer shell. Easily gains two electrons. Negative valence of 2.  $O^{2-}$



Fig 12—Metal Sodium (Na) One electron in outer shell. Easily loses one electron. Positive valence of 1,  $Na^{+}$

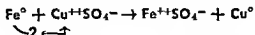
valeoce. The oxygen diagram shows the valence electrons of a typical nonmetal (Fig 11).

On the other hand, there are over fifty elements each of which has less than half of the electrons needed to fill out its outer atomic shell of eight. They give up their electrons easily during chemical change, to form positive ions. These elements are called *metals*. In general they unite with nonmetals to form salts, they decompose acids, and they unite with oxygen to form basic anhydrides, i.e., their hydroxides are bases. The diagram above is that of sodium, a typical metal (Fig 12).



### Listing Metals According to Their Activity:

The chemical activity of metals depends upon the ease of their atoms to ionize, and since *this ability varies* it is possible to arrange the metals in the order of decreasing activity. This partial series of metals, with the inclusion of hydrogen, is referred to as the Activity or Displacement Series (p. 145) because of the ability of each element to replace the metals below from their salts. Thus an iron nail will replace copper in a copper sulfate solution.



A glance at the Activity Series shows the feasibility of using aluminum vessels to hold solutions of those salts above it, of using chromium or nickel plated instruments to handle common salt (NaCl) and Epsom salt (MgSO<sub>4</sub>) dressings or packs, and of using vessels made of aluminum, zinc, or iron when cooking foods containing salts of those metals above them. On the other hand, avoidance or caution must be exercised in using solutions of salts of those metals below the above mentioned metals. For instance, aluminum vessels should not be used to hold iron solutions, chromium or nickel plated instruments should not be left in contact for any appreciable time with hydrochloride of mercury (HgCl<sub>2</sub>) or silver nitrate solutions, and lastly similar precautions must be kept in mind when cooking foods which contain iron, such as spinach, in aluminum vessels.

The position of hydrogen is noteworthy. All metals above it are very active, especially those at the top, and at some temperatures can replace hydrogen in water, acids, and many other compounds containing hydrogen. On the other hand, those metals below hydrogen are not so active, do not liberate molecular hydrogen from acids, can be acted upon only by oxidizing acids (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>), may occur uncombined in nature, are easily extracted from their ores, and ordinarily do not corrode. It is the lack of chemical

#### ACTIVITY SERIES (Partial List)

Potassium  
Calcium  
Sodium  
Magnesium  
Aluminum  
Zinc  
Chromium  
Iron  
Cobalt  
Nickel  
Tin  
  
Hydrogen  
Copper  
Mercury  
Silver  
Platinum  
Gold

activity or the resistance to corrosion (oxidation) that makes certain metals desirable in the home, hospital, and in industry. Articles made from them make a good appearance and preserve their usefulness over a long period of time. In estimating the usefulness, we must not fail also to consider their physical properties: *luster*, as the shining qualities of silver, *malleability*, or the ability to be hammered out into thin sheets, as gold leaf, *ductility*, or the ability to be drawn out into wire, as platinum, *hardness*, or the resistance to permanent change of form, as chromium, *conductivity of heat*, as aluminum, and the *conductivity of electricity*, as copper. The physical properties of the familiar metals as well as their resistance to wear and corrosion determine their usefulness.

### Tarnishing of Metals

Most metals become discolored or tarnished, either after being used or exposed to moist air. In the latter case, the tarnish generally is due to the formation of an insoluble oxide, such as that formed on iron, lead, aluminum, zinc, and nickel. Sometimes the tarnish is due to the action of oxygen, carbon dioxide, and moist air as the formation of a carbonate upon copper, or alloys containing copper (brass, bronze). At ordinary temperature, tin and silver do not become coated with a noticeable tarnish, but silver in the presence of sulfur or sulfur compounds, as hydrogen sulfide in the air or the sulfur in egg yolk and other foods containing sulfur compounds, darkens because of the formation of black, insoluble silver sulfide. The tarnish or rust on iron is generally considered as the hydrated form of iron oxide ( $2 \text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ ).

In addition to the tarnish consisting of oxides, carbonates, and sulfides, it is also well to consider the presence of grease, especially in the case of kitchen utensils.

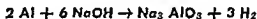
### General Methods of Removing Tarnish

Both acids and alkalis remove grease and some types of tarnish, but they cannot be used on all metals. Grease is readily dissolved from metals by naphtha or gasoline without any injury to the metals. Tarnish may be removed conveniently by scouring with abrasive material, care being taken not to use any abrasive that will scratch the metal. These abrasives include *infusorial earth* (siliceous earth) for scouring soaps and powders, *whiting* (chalk) for polishing silverware, and *steel wool* with good soap suds for kitchen utensils (except those of tin).

## Cleaning of Some Common Metals

Cleaning in the hospital is a most important factor since it includes the proper maintenance of cooking utensils, surgical instruments, furniture and other metallic materials. Methods for cleaning and polishing of some common metals follow.

**ALUMINUM** This is the most interesting metal used in the home. It is characterized by being very light in weight and having a silvery white color, the dullness usually associated with aluminum articles is the result of a thin coating of the oxide, which prevents any further tarnishing of the metal. This oxide tarnish may be removed by cooking an acid food in the aluminum vessel, or by allowing vinegar to stand for several hours in the vessel. Since aluminum dissolves and darkens in contact with alkaline solutions, washing soda or strong alkalis cannot be used for cleaning aluminum ware.



Because aluminum is durable, attractive in appearance, light in weight, easy to clean, an excellent conductor of heat, almost unchanged in air or water at ordinary temperature, and not affected by common foods, this metal is extensively used in making many kitchen utensils.

Before leaving the subject of aluminum it might be well to call attention to the compound sodium aluminum sulfate (alum), which is used in making certain brands of baking powder. This compound ( $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) hydrolyzes in water to form an acid which reacts with the sodium bicarbonate present to liberate carbon dioxide. The so called combination baking powders usually contain this compound and mono calcium phosphate as the acid forming ingredients which react with the baking soda to liberate carbon dioxide. All baking powders are a mixture of sodium bicarbonate (baking soda) and a solid acid or acid salt ( $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{KHC}_4\text{H}_4\text{O}_6$ ).

**IRON** Upon oxidation in moist air, iron forms scales of rust ( $2 \text{ Fe}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$ ), which peel off and expose a new surface for further corrosion. The amount of iron lost yearly in this way is enormous, the estimation being over 15 per cent of that produced. To protect iron from rust and corrosion it is covered with some resistant substance as paint, or enamel (glass glaze), the latter substance is widely used in making cooking utensils. Iron and enamel may be cleaned with abrasives containing alkalis.

Most of the iron used today is an alloy of iron called steel, which contains varying amounts of carbon up to 0.2 per cent and traces of other elements, the amount used depending upon the intended use of the steel. Of the many steel alloys the most interesting are those first introduced as *stainless* kitchen utensils, but which are now used in the manufacture of stoves, plumbing fixtures, refrigerators and even in the surfacing of buildings (Empire State, New York City) for protection against corrosion. Such steels contain chromium and a small amount of nickel or cobalt.

Iron also may be protected from rust or corrosion by coating it with more resistant metals, the most important of which are tin, nickel, chromium, zinc, silver, and gold.

**TIN** This is extensively used to cover iron and make the familiar tin cans in which foods are preserved. Some tinware is still used to make kitchen utensils. The metal is very resistant to the formation of tarnish, and to the action of food acids or weak alkalis. Tinware can be cleaned and polished with soft abrasives containing weak alkalis (washing soda).

**NICKEL** This is often used to plate steel articles because of its hardness and ability to take a high polish which slowly diminishes in moist air. It is for this latter reason that *chromium* is largely replacing nickel plating. Both of these metals may be cleaned and polished by the same abrasives used on tin.

**SILVER** This is a soft metal capable of a high polish. Its tarnish usually is due to the formation of black silver sulfide which may be removed by a soft abrasive containing ammonia water. The tarnish may be removed more easily by placing the silverware in contact with aluminum in a vessel containing a warm solution of washing soda and salt. Since aluminum vessels become stained it is better to use an enamel pan containing a piece of aluminum.

**ZINC** Coating iron with zinc protects the iron from corrosion because the thin layer of zinc oxide or carbonate formed on exposure to air sticks and prevents any further action. Iron coated with zinc is called galvanized iron, a very familiar product in buckets, garbage cans, wire, and similar articles. Cleaning is accomplished by the use of ordinary abrasives and soap.

**GOLD** This metal is not acted upon by air, moisture, or the common acids. However, in alloying it with copper to increase its hardness, the gold in common use tends to become tarnished. A very soft abrasive, preferably one containing ammonium hydroxide, cleans and polishes gold articles.

In medicine a colloid prepared from gold chloride is used to aid in diagnostic tests on cerebrospinal fluid. Normal fluid in serial dilution does not alter the shade of the beautiful salmon color of colloidal gold when it is mixed with it. Spinal fluid from patients with meningitis, poliomyelitis and various stages of syphilis, etc. gives definite color changes ranging from the original salmon to purples and colorless in dilutions of a series of spinal fluid concentrations—a gold curve.

### SELF-TESTING QUESTIONS

- 45 What is a metal?
- 46 What is noteworthy concerning the position of hydrogen in the replacement series?
- 47 What does the usefulness of the common metals depend upon?
- 48 What is the nature of tarnish?
- 49 How in general may tarnish and grease be removed from metals?
- 50 What precautions must be used in cleaning aluminum?
- 51 What is the composition and what are the uses of stainless steels?
- 52 Why is chromium plating replacing nickel plating?
- 53 How may silverware be easily cleaned?
- 54 What is galvanized iron?

## VI ALLOYS OF METALS

### Nature of Alloys

In using the term metal, we usually think of pure metallic elements, as copper and aluminum. A study, however, of the familiarly used metals shows the very surprising fact that the great majority of them are composed of two or more pure metals melted together into what is called an *alloy*. The art of making alloys is very old, and was practiced during an early period of human progress (Bronze Age). The variations in their composition and resulting properties indicate that alloys are not always mixtures or true solutions of elements, but may consist of solutions of definitely formed compounds, or all of these together.

### Properties of Alloys

The properties of alloys are quite different from those of the original metal constituents. As a general rule, alloys, as compared to their constituents, have low melting points, such as the fusible alloys for automatic sprinklers, they have different colors as green and white gold, less electrical conductivity as the resistance wires in electrical toasters, greater resistance to corrosion as stainless

## SOME COMMON ALLOYS

Name	Composition	Properties (Distinctive)	Uses
Brass	Cu 60-80 Zn 20-40	Resists corrosion	Castings
Bronze	Cu 70-95 Sn 1-18	Hard noncorroding	Ornaments statues
Monel Metal	Cu 27 Ni 68 Mn & Fe 5	Resists corrosion	Acid resisting containers
Aluminum Bronze	Al 2-10 Cu 90-98	Hard gold or silver color	Ornaments imitation gold
Duralium	Al 95 Cu 3 Mn 1 Mg 0.5	Light noncorrosive	Aircraft parts
Magnalium	Al 90-94 Mg 2-10	Light noncorrosive	Castings aircraft
Gold Coin	Au 90 Cu 10	Yellow color permanence	Coins jewelry
Green Gold	Au 60 Ag 35 Cu 5	Beauty	Jewelry
Gray Gold	Au 20 Pd 80	Beauty	Jewelry
White Gold	Au 15 Pd 85	Beauty	Jewelry
Silver Coin	Ag 90 Cu 10	Beauty permanence	Coin jewelry
Sterling Silver	Ag 92.5 Cu 7.5	Beauty permanence	Jewelry
Durron	Fe 85-88 Si 12-15	Resists corrosion	Acid containers
Stainless Steel	Fe 74 Cr 18 Ni or Co 8	Noncorrosive	Kitchen utensils
Nickel Coin	Ni 25 Cu 75	Beauty noncorrosive	Coins
Solder	Sn 75 Pb 25	Melts at low temperature and sticks	Soldering
Wood's Metal	Bi 50 Pb 25 Sn 12.6 Cd 12.5	Low melting point	Safety fuses
Pewter	Sn 85 Sb 15	Soft	Tableware utensils

steel, and they are harder, as is the chromium nickel steel used in making armor plate

There are many thousands of alloys, of which the most important is steel. The previous table lists some common alloys, their composition, properties, and uses.

## SELF-TESTING QUESTIONS

- 55 What is an alloy?
- 56 What may determine the properties of alloys?
- 57 What are five general properties of alloys?
- 58 What is the most important alloy?

## SUGGESTED ACTIVITIES

## I. THOUGHT PROVOKING QUESTIONS

- 1 What properties of ammonia make it suitable for use in the preparation of manufactured ice?
- 2 State briefly the physical and chemical ways in which the halogens resemble each other.
- 3 Explain how Dakin's solution is used, and what chemical action takes place in using the solution.
- 4 What substances already studied are used as bleaching agents? What chemical properties do they possess in common?

- 5 Name five elements that exist in allotropic forms
- 6 Explain how chlorine is used in the disinfection of water supplies
- 7 Explain how the burning of sulfur serves to disinfect a room
- 8 Name a medicinal use of a specific ammonium salt, nitrate, chloride, bromide, iodide, sulfate, phosphate, and carbonate
- 9 What are the properties of chlorine that made it suitable for gas warfare?
- 10 What might be the hazard of congested motor traffic in a tunnel?
- 11 The cost of solid carbon dioxide is approximately 25 times the cost of ordinary ice. How do you account for its use?
- 12  $\text{CO}_2$  is a respiratory stimulant, however, too much  $\text{CO}_2$  re-breathing has what disadvantage? What does the re-breathing of  $\text{CO}_2$  interfere with?
- 13 How may carbon monoxide find its way into the home?
- 14 Why not prepare nitrogen by burning a candle in the air?
- 15 Give the name and formula for a compound of nitrogen in which nitrogen has a valence of 3, of 5
- 16 Explain why dry ammonia does not affect litmus paper
- 17 Why may ammonium salts be used as smelling salts?
- 18 What variety of phosphorus is used in the manufacture of safety matches? In the manufacture of rat poison?
- 19 Name an element acting as a metal in a definite compound, and as a nonmetal in another compound
- 20 Zinc is higher than iron in the replacement series. Why is it used for coating iron?
- 21 Write the reactions between alum and baking soda

## II VOCABULARY TESTING OF NEW TERMS

nitrifying bacteria	halogen	choka damp
nitrogen cycle	allotropic	photosynthesis
amphoteric	amorphous	alloys
metal	destructive distillation	nitride
nonmetal	carbide	fluoridation

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Composition of Inspired and Expired Air
- 2 Invention and Development of Matches
- 3 The Fixation of Nitrogen
- 4 Medicinal Applications of the Halogens
- 5 The Status of Water Fluoridation in My Community
- 6 Dangers of Carbon Monoxide Poisoning

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**TO THE INSTRUCTOR** The laboratory time may well be used this week for either oral or written work, making a general survey of the fundamentals of the inorganic chemistry taught

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## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 693, 695, 696, 698, 700

# X RAYS, RADIOACTIVITY, AND NUCLEAR CHEMISTRY

## CHAPTER OUTLINE

- |   |   |
|---|---|
| <b>I X RAYS</b><br>(a) Discovery and nature of x rays<br>(b) Use of x rays  | <b>IV ARTIFICIAL RADIOACTIVITY</b><br>(a) Production of radioisotopes<br>(b) Radioisotopes in medicine and nutrition  |
| <b>II RADIUM AND RADIOACTIVITY</b><br>(a) Discovery and properties of radium<br>(b) Nature of radioactivity<br>(c) Uses of radium | <b>V NUCLEAR ENERGY</b><br>(a) Source and magnitude of nuclear energy<br>(b) Splitting the uranium nucleus<br>(c) Plutonium<br>(d) Hydrogen bomb<br>(e) Physiological effects |
| <b>III NUCLEAR REACTIONS</b><br>(a) Nature of nuclear reactions   |   |

## I. X RAYS

## Discovery and Nature of X rays:

Roentgen in the year 1895 observed that the passage of an electrical discharge through a highly evacuated Crookes' tube produced an unusual type of radiation. This type of radiation, now known as the x ray, is generated when rapidly moving electrons strike a massive target. The essentials of an x-ray tube are shown

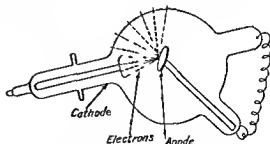


Fig 1—X ray Tube A stream of electrons bombards a dense medium to provide x rays. Why is the tube highly evacuated?

in Fig. 1. When such an evacuated tube is operated under a high voltage, electrons stream across the tube from the concave cathode and bombard the anticathode or target. The impact of the electrons (cathode ray) on atoms of the target gives rise to the x radiation. Such rays are in many respects similar to ordinary light



rays. The fundamental point of difference is in the fact that x rays have much shorter wave lengths

### Use of X rays:

X rays are in themselves invisible, yet they cause many substances to fluoresce or to glow and become luminous. By reason

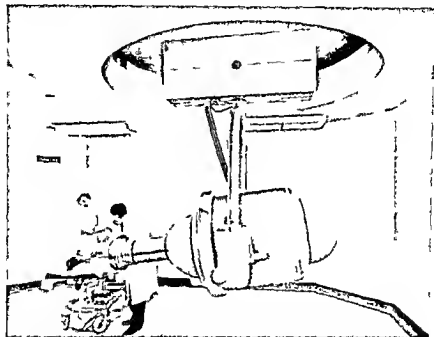


Fig 2—X ray Therapy Treatment View of a 1,000,000 volt x ray unit being positioned for treatment. What factors determine the length of time for a treatment? Courtesy, General Electric Company

of their very short wave lengths, x rays are able to pass through many substances, for example flesh, which are opaque to ordinary light. More dense objects such as bones and metals largely stop the radiation and in this way produce shadows. This makes it possible to prepare x-ray photographs (roentgenograms) which are of considerable aid to the physician. A bone fracture can be studied, or a piece of metal, such as a bullet, can be located in the flesh. Barium sulfate is opaque to x rays and when a water suspension of this salt is administered by mouth or rectum it coats the inner

surfaces of the stomach and intestinal tract, this makes it possible to secure x ray photographs of these organs

More recently x ray tubes have been developed to operate under very high potentials, frequently greater than 1,000,000 volts X rays generated in such tubes are referred to as "hard" rays, and are highly penetrative In fact they resemble the gamma radiation which is emitted by radium and other radioactive elements during their process of decay Short wave length x rays are in many instances replacing the gamma rays for the treatment of skin disorders, cancer, and other types of pathological tissue

## II. RADIUM AND RADIOACTIVITY

### Discovery and Properties of Radium\*

Within a year after the discovery of x rays the scientist Henri Becquerel found by accident that compounds of uranium undergo a spontaneous disintegration in the course of which radiations are emitted In one of his experiments Becquerel placed a piece of a compound of uranium on a photographic plate which was wrapped light tight in black paper When the plate was developed, it was evident that the uranium compound was giving off a type of radiation which, like the x ray, affected the photographic plate Thus the specimen of uranium compound had taken its own picture

At Becquerel's suggestion the French physicists Pierre and Marie Curie undertook the task of investigating further the source of this radiation After months of intensive research they were able to announce the discovery of two new elements, namely polonium and radium Radium was discovered in 1898 in the form of a compound, it was not until 1910, however, that Madame Curie\* succeeded in isolating the metallic element itself Radium was so named because of its radiations (giver of rays) and polonium was named after Poland Madame Curie's native country Radium occurs in minute quantities in all uranium ores (carnotite, pitch blende) hence tons of raw material must be worked over and carried through long processes of concentration by successive fractional crystallizations, to isolate a few grams of a radium compound At the present time ores from the Belgian Congo and from the Great Bear Lake region in Canada are the main sources of radium

\* Madame Curie died at the age of 67 of aplastic pernicious anemia brought on by a long accumulation of radiations Pierre Curie was killed in a Paris street accident in 1906

The amount of this element which has been produced to date in the form of its salts such as the insoluble sulfate, is estimated as nearly 1,000 grams, priced at about \$25,000 per gram

Investigators found radium to have strange properties. It gave off energy continuously in the form of radiations and heat, affected the photographic plate, glowed in the dark, ionized the air around it, caused zinc sulfide and many minerals to exhibit fluorescence and most noteworthy of all, killed bacteria and burned animal tissue placed near by. This property of natural, spontaneous disintegration, exhibited by radium and a number of other elements, is termed natural radioactivity. Neither chemical combination nor physical treatment affects the radioactivity of such elements.

### Nature of Radioactivity

A thorough study by Rutherford and others has shown that radium and other naturally radioactive elements emit three types of rays namely the alpha, beta, and gamma radiations. The alpha

RAYS FROM RADIOACTIVE ELEMENTS

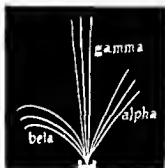
Radiation	Absorbed by	Relative penetration	Velocity
Alpha ( $\alpha$ ) Positive charge	Writing paper or 6 cm. of air	1	10 000-20 000 miles per second
Beta ( $\beta$ ) Negative charge	1 mm. of lead or equivalent	100	About 100 000 miles per second
Gamma ( $\gamma$ ) No charge	13 cm. of lead	10000	186 000 miles per second (speed of light)

radiation consists of a stream of particles which are helium nuclei. The nucleus of the helium atom is made up of two protons and two neutrons hence such particles carry positive charges and consequently are deflected when passed between oppositely charged plates or the poles of a magnet. The beta radiation is made up of particles which prove to be electrons identical with the electrons of the cathode ray in the x ray tube. Such particles are of negative charge and therefore when the beta radiation passes between the

poles of a magnet it is deflected in a direction opposite to that of the alpha radiation

The gamma rays are similar to light rays, but have a much shorter wave length. Gamma rays resemble hard x rays. This radiation is not deflected in a magnetic field which is proof that it carries no charge. Gamma rays have a high power of penetration. Light, radio communication rays, x rays, and gamma rays are all electromagnetic disturbances of different wave lengths.

Fig. 3—Radium Rays. The gamma rays have the greatest speed. The alpha and beta rays are bent in opposite directions in the presence of a magnet. What does this prove about gamma rays? Courtesy Dynamic Chemistry. Rand McNally.



The reader must not conclude that the radioactive elements disintegrate completely into the radiations just described. When the nuclei of radioactive atoms lose alpha and beta particles, new elements result. The immediate successor of radium is an element named radon or radium emanation. Radon is a member of Group O of the periodic classification and, like helium and other members of this group, radon is a chemically inert gas. Nevertheless, this element is in itself highly radioactive and emits penetrating gamma rays.

During radioactive disintegrations, enormous quantities of heat are liberated. In the case of radium, one gram gives off 137 calories per hour. This heat is generated by collisions of alpha and beta particles with surrounding molecules.

Rutherford and Soddy have advanced the theory that radium is one member of a series of radioactive elements which begins with uranium I and terminates in an inactive isotope of lead. In addition to this series there are two others. One of these, the actinium series, is likely a branch of the uranium I series. The third series begins with thorium and, like the others, ends with an isotope of lead. The uranium series is presented in the table which follows.

## THE URANIUM DISINTEGRATION SERIES

Element	Atomic Weight	Atomic Number	Radiation Emitted	Half life Period
Uranium I	238	92	$\alpha$	$4.67 \times 10^9$ yrs
Uranium X <sub>1</sub>	234	90	$\beta$	24.5 days
Uranium X <sub>2</sub>	234	91	$\beta$	1.14 minutes
Uranium II	234	92	$\alpha$	$2 \times 10^5$ yrs
Ionium	230	90	$\alpha$	$7.6 \times 10^4$ yrs
Radium	226	88	$\alpha$	1590 yrs
Radon	222	86	$\alpha$	3.85 days
Radium A	218	84	$\alpha$	3.05 minutes
Radium B	214	82	$\beta$	26.8 minutes
Radium C	214	83	$\alpha\beta$	19.7 minutes
99.97% $\swarrow$ Radium C	214	84	$\alpha$	$1 \times 10^{-6}$ sec
0.03% $\searrow$ Radium C	210	81	$\beta$	1.32 minutes
Radium D (radiolead)	210	82	$\beta$	22 years
Radium E	210	83	$\beta$	5.0 days
Radium F (polonium)	210	84	$\alpha$	140 days
Radium G (lead)	208	82	—	stable

*Loss of an alpha particle (nucleus of a helium atom) decreases the atomic weight by four units and lowers the atomic number by two units. Loss of a beta particle (electron) has no appreciable effect on the atomic weight, but increases the atomic number by one. The gamma radiation which accompanies loss of alpha and beta particles causes no change in either atomic weight or atomic number. A number of the elements listed in the series are in reality isotopes. For example, radium B, radium D, and lead all have the same atomic number of 82, and hence are isotopes of lead. It is to be recalled that all isotopic forms of a given element have the same atomic number, but differ in atomic weight. Because of the existence of isotopes we now define an element as a pure substance, all of whose atoms have the same atomic number.*

## Uses of Radium

Shortly after the discovery of radium those experimenting with its compounds, such as the bromide and sulfate, began to develop cutaneous sores which proved to be extremely difficult to heal. Investigation showed that the radioactive rays would also destroy bacteria and other similar organisms much more rapidly than they

would injure healthy tissue. This property of radium makes it useful in the treatment of disease, notably ringworm, cancer, and other growths. Radium has proven effective in the treatment of many skin diseases, chronic infections, and to some extent in reducing scars.

Research indicates that malignant cells in their very rapid growth are particularly sensitive to the rays, and, as a consequence, radium may be used to inhibit or destroy the growth of those pathogenic cells, which are cancer cells and grow and multiply rapidly. Of the many varieties of cancer the rapidly growing type can be most successfully treated with x rays and gamma rays. In some cases the greatest benefit may come from combined surgery and ray treatment. To a certain extent, healthy tissue may be injured, particularly if the exposure to radiations is too frequent or prolonged. For this reason, in radium therapy an attempt is usually made to protect healthy tissue from the destructive action of the radiations by the use of shields which are impervious to the rays. Lead metal may be employed for this purpose. The objective in the use of radium is to produce the greatest amount of destructive action on pathogenic cells with the least possible injury to the normal cells of the body. Radium is kept in steel horns which are lined with lead to prevent the escape of the penetrating, destructive radiations. It has been observed that the absorption of radium compounds in the body is dangerous, since these compounds tend to accumulate in the bones and disintegrate them.

In addition to its therapeutic uses, minute quantities of radium, mixed with fluorescent substances (zinc sulfide), have an application in making luminous enamels and varnishes for watch and clock bands, instrument dials, and other small objects which it is desirable to have luminous in the dark. Mesothorium, a disintegration product from the radioactive element thorium, is to some extent replacing the use of radium for such luminous preparations.

In some hospitals the radioactive gas radon (radium emanation), which is formed by the disintegration of radium, is used in place of the more expensive radium. The radon is sealed in short needle-like tubes of glass or gold, called "seeds," which can be inserted directly into malignant growths. The lower cost, intensity of radiation, and the ease with which radon tubes may be imbedded in a malignant growth or applied to a limited area make this radioactive gas very suitable for therapeutic purposes. However, radon is rather short-lived and loses one-half of its activity in 3.85 days. In contrast, radium has a half-life period of 1590 years.

It should be quite obvious that safe and successful radiotherapy demands a high degree of knowledge, skill, and experience. Serious if not fatal injury may result from x rays and radioactive materials in the hands of the careless or inexperienced operator.

### SELF-TESTING QUESTIONS

1. How are x rays produced?
2. Describe the experiment of Becquerel which led to the discovery of radium.
3. Define natural radioactivity and describe the rays given off by radioactive elements.



Fig. 4—An x-ray unit being positioned for x-ray therapy. Observe the painstaking care being exercised for proper positioning. Courtesy General Electric Company.

- 4 Select several sets of isotopes from the uranium I disintegration series, other than the case already given as an illustration
- 5 What radiation from radium is effective in its therapeutic applications?
- 6 What precautions are necessary in the use of radium?
- 7 Tell how radon is obtained and in what way it may be used
- 8 Just why is it possible in many cases to substitute x ray treatment for radium treatment?
- 9 Define or explain the following isotope, radium emanation, half life period

### III. NUCLEAR REACTIONS

#### Nature of Nuclear Reactions:

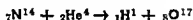
The nuclei of atoms are made up of protons, neutrons, alpha particles, and possibly other structural units. It would seem possible therefore, that bombardment with fast moving particles could

#### IMPORTANT PARTICLES IN NUCLEAR STRUCTURES

<i>Particle</i>	<i>Approximate Mass</i>	<i>Charge</i>	<i>Symbols</i>
Proton	1	+1	$+$ , $p$ , ${}_1p^1$ , ${}_1H^1$
Electron	0.00055	-1	$-$ ; $e$ , $\beta$ , $-1e^0$
Positron	0.00055	+1	$\beta^+$ , $+1e^0$
Neutron	1	0	$n$ , ${}_0n^1$
Alpha particle	4	+2	$\alpha$ , ${}_2He^4$

dislodge such structural units from the nucleus. Scientists have been successful in doing this. By employing machines such as the electrostatic generator and the cyclotron, charged particles like the proton, alpha particle, and deuteron (nucleus of deuterium) can be accelerated to very high velocities. Such powerful missiles have been used to disintegrate practically every element. The particle which strikes the nucleus becomes at least momentarily a part of it; a nuclear reaction may then occur with the formation of new nuclei. Such nuclear reactions might be described as transmutations, a dream of alchemists in the very early history of chemistry.

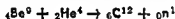
One of the first reactions of this type to be studied was the bombardment of nitrogen with alpha particles. This nuclear reaction is illustrated with an equation not unlike a chemical equation



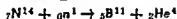


The superscript above and to the right of each symbol shows the atomic weight. The atomic number is given by the subscript below and to the left of the symbol. Thus, when an alpha particle (nucleus of the helium atom) strikes the nucleus of a nitrogen atom a reaction occurs which results in an oxygen atom of mass 17, and a hydrogen nucleus (proton). The alpha particles ( ${}^4_2\text{He}$ ) for this reaction are shot out of the nuclei of certain radioactive atoms in the course of their natural disintegration. The number of nuclear hits in this type of bombardment, compared to the number of masses, is very small, only about 1 alpha particle in 10,000 strikes a nitrogen nucleus.

Another very effective bombarding particle is the neutron. Since this particle carries no net charge it is not repelled by a positive nucleus or by the planetary electrons around a nucleus. A great many nuclear reactions have been carried out with the neutron as the bullet for penetrating the target. Neutrons for such processes are produced in certain nuclear transformations as typified by the following



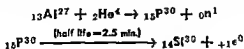
In this transmutation, alpha particles have been employed to convert beryllium of mass 9 into carbon of mass 12. The neutrons ( ${}^1_0\text{n}$ ) released in the process become in themselves excellent projectiles for subsequent nuclear changes. One such transformation occurs when nitrogen is bombarded



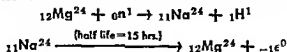
#### IV. ARTIFICIAL RADIOACTIVITY

##### Production of Radioisotopes:

In 1934 Irene Curie Joliot, daughter of Madame Curie, and M. Joliot observed that some of the lighter elements such as boron, magnesium, and aluminum became radioactive after bombardment with alpha particles. When the bombardment ceases the product is found to have a short lived activity, which is characterized as artificial or induced radioactivity. As an illustration, when aluminum is bombarded with alpha particles a radioactive isotope of phosphorus with a mass of 30 results. This isotope decays rapidly, having a half life period of 2.5 minutes. The formation and decay of radioactive phosphorus are expressed in the following equations



An interesting case is the transmutation of magnesium into a radioactive isotope of sodium. The sodium has a half-life period of approximately 15 hours, and by loss of a beta particle, reverts to the original magnesium. This is summarized in the following nuclear equations:



Over 800 artificially radioactive isotopes have been prepared from stable isotopes by nuclear reactions similar to the ones illustrated.

### Radioisotopes in Medicine and Nutrition:

Chemically and biologically, radioisotopes behave like their stable isotopes, but differ in that they can be detected, even in minute



Fig 5—Geiger counter used by man at left to keep a check on radioactivity while a small amount of radioiodine is being withdrawn for placement in small flask at right. Why is flask walled off by the lead bricks? Courtesy of University of Chicago.

quantities, with the electroscope (Geiger counter), an instrument which is sensitive to radioactivity. This provides a method for tracing and studying chemical reactions taking place in the body. Thus, if a trace of radioactive calcium is added to the food it becomes possible to determine where the calcium is deposited in the body. Many interesting and valuable facts concerning the complex chemical reactions of life processes have been brought to light.  $^{32}_{15}\text{P}$ , a radioactive isotope of phosphorus, prepared by nuclear bombardment, and having a half life period of about 14 days, is used in chronic leukemia (lymphatic, myeloid) studies in which condition the white cells become too numerous. The circulation of the blood can be studied by the intravenous injection of radio sodium in the form of sodium chloride, in surgery the rate of circulation may be the deciding factor in cases where amputation seems necessary. It is now known from investigations with radioactive iron that the human system in normal health retains its iron, absorbing and excreting little, but in an anemic condition iron is absorbed rapidly. Use of a radioactive isotope of iodine (iodine 131) as a "tagged atom" makes possible a study of the function of iodine in diseased thyroid glands. Radiocarbon ( $\text{C}^{14}$ ) will undoubtedly prove to be a useful tool in biochemistry for learning more about the fate of carbohydrates, fats, and proteins in digestion and metabolism.

Cobalt 60 is an active source of powerful gamma rays, and it is used today in much the same way as radium and radon. Compared to radium, cobalt 60 is cheaper and easier to manipulate, and its gamma radiation is more homogeneous.

In overactivity of the thyroid gland, Graves' disease for example, the highly selective power of the thyroid gland for iodine ( $\text{I}^{131}$ ), with the ensuing disintegration of the iodine isotope into beta and gamma rays to destroy overactive tissues, has benefited patients. Use of radioiodine to determine thyroid function can serve as an indication of a patient's metabolic state. All of this is a tribute to atomic medicine.

Such radioisotopes as  $\text{C}^{14}$ ,  $\text{P}^{32}$ ,  $\text{S}^{35}$ , and  $\text{Ca}^{45}$ , all of which have half life periods greater than 12 days, have been made available to research organizations, hospitals, clinics, and medical colleges for therapeutic and tracer applications. In the field of medicine and nutrition it is likely that such isotopes will find their greatest use not as therapeutic agents but rather as tools for tracing disease and studying biochemical reactions. Thus the discovery and availability of radioactive isotopes have thrown open an entirely

new field of investigation with special significance in biochemistry

Some radioisotopes which have use in medicine and in biochemical research are listed here

<i>Name</i>	<i>Half life</i>
Calcium 45	180 days
Carbon 14	5740 years
Cobalt-60	5 2 years
Iodine 131	8 days
Phosphorus 32	14 7 days
Sodium 24	15 hours



Fig 6—The atom c bomb hit on Nagasaki heralds a new age of power from the atom (Acme Photo)

## V. NUCLEAR ENERGY

The large scale release of nuclear energy was revealed in the use of atomic bombs in 1945. This came as the culmination of several decades of research, greatly intensified in the last few years by the pressure of war. The terrible destruction wrought in the cities of Hiroshima and Nagasaki is ample proof of the enormous quantity of energy set free in atomic disintegration.

### Source and Magnitude of Nuclear Energy

The energy of ordinary chemical reactions is associated with the whirling, planetary electrons which occupy space beyond and around the compact, highly dense nucleus of the atom. In the processes of combustion of coal and explosion of gunpowder the energy released is restricted to forces outside the nuclei, the nuclei themselves remain intact. The far greater energy stored in the nucleus is released only when bombarding particles invade it, and break down the enormous forces binding together protons and neutrons. The magnitude of this nuclear energy can better be appreciated when it is realized that one pound of uranium 235, an isotope of the element uranium, upon nuclear disintegration (fission) will liberate energy equivalent to that released by burning 1500 tons of coal. Stated in another way, one gram of this same isotope will release energy equivalent to 20 billion calories of heat. In the generation of such nuclear energy about one thousandth part of the original mass disappears to provide it. Many years before nuclear energy was tapped, Einstein had shown that matter can be converted into energy under certain extreme conditions. We are now led to the conclusion that matter is in reality a form of energy.

### ISOTOPES OF URANIUM

(Nuclear structures  $n$  = neutron,  $p$  = proton)

$\begin{array}{c} 92p \\ 146n \end{array}$	$\begin{array}{c} 92p \\ 143n \end{array}$	$\begin{array}{c} 92p \\ 142n \end{array}$
$U^{238}$	$U^{235}$	$U^{234}$
at wt = 238	at wt = 235	at wt = 234
at. no = 92	at no = 92	at no = 92
99.2%	0.7%	less than 0.01%

## Splitting the Uranium Nucleus:

Uranium, atomic number 92, has been the basis in the development of nuclear energy. Natural uranium ores, regardless of source, contain the three isotopes of the element in fixed proportions. These isotopes are designated as  $U^{238}$ ,  $U^{235}$ , and  $U^{234}$ , and are present to the extent of approximately 99.2 per cent, 0.7 per cent, and less than 0.01 per cent respectively.

$U^{235}$  has been used directly as a source of nuclear energy. Another isotope  $U^{238}$ , which constitutes over 99 per cent of all natural uranium, is used as the raw material for the synthesis of an element named plutonium. Like  $U^{235}$ , plutonium has proved to be a valuable source of energy.

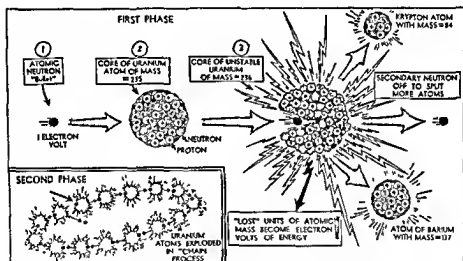
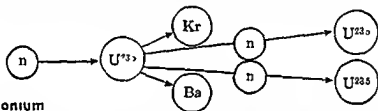


Fig. 7—How The Atom Is Split. Modified drawing appearing in American Weekly, Issue of Sept. 3, 1945.

The separation of  $U^{235}$  from its more stable isotope,  $U^{238}$ , is not possible through chemical reactions inasmuch as all isotopes of a given element exhibit identical chemical behavior. It has been necessary therefore to resort to physical methods of separation; methods which in this instance are based on the slight difference in mass of the two isotopes. A discussion of these procedures is beyond the scope of this book; suffice it to state that methods employing gaseous diffusion, the principle of the centrifuge, the use of the mass spectrograph (electromagnetic method), thermal diffusion, and others have been investigated and used with varying degrees of success. All are laborious and time consuming. Scientists who

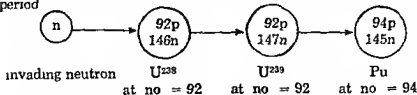
developed the atomic bomb necessarily gave considerable attention to the problem of separating the rather rare  $U^{235}$  from the more abundant  $U^{238}$

When the nucleus of a  $U^{235}$  atom is invaded by a relatively slow moving neutron, fission of the nucleus occurs, with the formation of lighter atoms. Also important is the release of nuclear energy and several neutrons. Such neutrons become projectiles for splitting additional  $U^{235}$  nuclei. The fission process in a sense provides its own ammunition, and in this way a self sustained or chain reaction may be set in motion. If conditions are such that the number of effective neutron impacts on  $U^{235}$  nuclei progressively increases, and the heat is not dissipated as rapidly as generated, the process will attain explosive proportions as it does in the atomic bomb. There are a number of possibilities in the fission of  $U^{235}$  nuclei, one of the more usual is pictured as follows

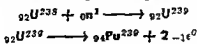


### Plutonium

Another approach in the release of nuclear energy has been the preparation of a new element, plutonium from  $U^{238}$ . Inasmuch as plutonium is not an isotope of uranium, but a distinct element, it becomes possible to separate it by chemical methods. The procedure for its synthesis is the bombardment of  $U^{238}$  with neutrons to produce unstable, short lived  $U^{239}$ . This isotope of uranium, artificial in character, upon loss of beta particles becomes the new man made element plutonium, atomic number 94. Plutonium is known as a trans uranic element and it has a very long half life period.



In equation form these changes are represented as follows



Another element named neptunium, atomic number 93 and hence a trans uranic element, is produced as an intermediate in the conversion of  $U^{238}$  into plutonium. This element is not represented in the preceding simplified picture.

The device used to produce plutonium from  $U^{238}$ , and at the same time control the rate of the reaction, is called a "pile." A pile is a combination of uranium and "moderator" such as carbon, it is constructed by placing rods of uranium in blocks of graphite. The graphite captures relatively few neutrons, but serves to slow them down from the velocities they attain in nuclear fission to a point where they are more likely to be captured by  $U^{238}$  nuclei or produce fission of  $U^{235}$ . Materials may also be incorporated in the pile to absorb neutrons harmlessly and prevent chain reactions from progressing too rapidly. The heat which is generated must be removed to prevent excessive temperatures. Piles, now commonly called nuclear reactors, are being constructed throughout the world to produce power. New submarines are driven by atomic power plants.

### Hydrogen Bomb

As has been noted, the process of nuclear fission, popularly referred to as "splitting the atom," releases tremendous quantities of energy. In more recent years it has been discovered that certain very light weight nuclei can be made to fuse into heavier nuclei with the conversion of mass into even greater concentrations of energy. This has led to the development of a hydrogen bomb which derives its energy from the fusion of hydrogen nuclei to produce helium nuclei. Considerable energy is needed to start the fusion, this energy may be provided by an initial fission process.

Nuclear fusions are going on in the sun, and this becomes the source of much of the energy which we receive from the sun's radiations.

### Physiological Effects

The effects of atomic bomb explosions on life have been studied at Hiroshima and Bikini, and in subsequent experimental explosions. The destruction of life is **not** due solely to the concussion set up by the explosion itself. Harmful radiations, such as neutrons and gamma rays, travel from the center of the explosion with speeds comparable to that of light. To the present time the only effective



measures for protection against such rays are heavy walls of steel, concrete, and similar massive materials, or considerable distance.

The gamma rays, in effect super x rays, are immediately destructive to life. The danger from neutrons is due to a secondary effect, since these particles impart artificial radioactivity to many elements. The sodium which is found throughout the body becomes radioactive under the impact of neutrons, and in such a state emits gamma radiations. The phosphorus which is an integral part of bones and certain tissues is another element made radioactive by bombardment with neutrons. Loss of white blood cells results, and the system has then little or no resistance to infectious disease. In studies conducted at Bikini, where experimental animals were exposed in the vicinity of the explosion, it was observed that in some cases the physiological effects were delayed for as much as two weeks. Thus the body after exposure to neutron radiation may become its own source of death.

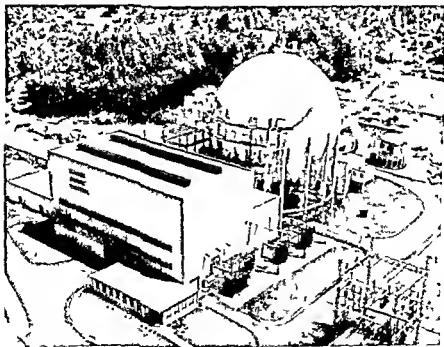


Fig. 8—Production of Electricity from Nuclear Energy. This pictures the most modern method of generating electricity. What are other peacetime uses of nuclear energy? Courtesy, of Yankee Atomic Electric Company.

The peacetime testing of atomic bombs and thermonuclear devices by exploding them in or above the atmosphere has been of grave concern to the governments and peoples of the world. The radioactive dusts created by the explosions are carried for hundreds of miles by the prevailing winds. Gradually the particles settle out of the atmosphere and over the surface of the earth to create a health hazard. Of particular concern has been the radioisotope called strontium 90, which has a half life of twenty seven years. Formed as a radioactive dust it settles in time and contaminates food crops and pasture lands. In the body, strontium 90 seeks out bone structure. When the atmosphere is known to be contaminated with radioactive debris it is a practice to periodically check the Sr 90 level in milk.

Without a doubt the release of nuclear energy is one of the greatest discoveries in recorded history, how it is used will no less certainly determine the fate of mankind. Science has placed in the hands of man untold power. If this is properly directed in peace time pursuits, much is promised for the welfare of the human race.

### **SELF-TESTING QUESTIONS**

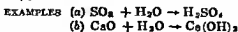
- 10 What are the projectiles which scientists have used for penetrating nuclei of atoms? What are sources of such particles?
- 11 How may charged particles be given greater velocities?
- 12 Name and describe the particles which are important in nuclear structures.
- 13 What is the distinction to be made between natural and artificial radioactivity?
- 14 Why is the separation of the isotopes of uranium restricted to physical methods?
- 15 Why can plutonium be separated from uranium isotopes by chemical methods?
- 16 Why is strontium 90 a potentially dangerous isotope?

### **SUGGESTED ACTIVITIES**

#### **I. THOUGHT PROVOKING QUESTIONS**

- 1 How does the energy of the ordinary chemical reaction compare with nuclear energy? What is the source of each?
- 2 Describe the production of radioisotopes and cite examples to show their importance in biochemistry.
- 3 Write an equation to illustrate the following nuclear transmutation: boron mass 10 disintegrated with an alpha particle yields an isotope of nitrogen mass 13 and a neutron.
- 4 Discuss the physiological effects of the radiations released in large scale nuclear disintegrations.

**anhydride** (an hidride) An oxide which on addition of water becomes  
(a) an acid or (b) a base



**anhydrous** (an hidrus) Without water

EXAMPLES Blue vitriol or washing soda after losing water of hydration

**anoxia** A condition in which the cells are not obtaining a sufficient supply of oxygen

**atom** The smallest particle of an element taking part in a chemical change

EXAMPLE The smallest particle of sodium that can combine with chlorine is an atom.

**base** A substance containing the group OH, the water solution of which gives hydroxyl ions



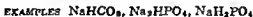
**basic salt** A compound formed when only part of the hydroxide radicals of a base are replaced by the acid radical of an acid



**binary acids** (bi na re) Acids containing hydrogen and one other element



**buffer salts** Salts in the blood which counteract the action of acids or bases



**calorie** (small) The unit of heat which is required to raise the temperature of one gram of water one degree centigrade

**catalytic agent** (ket al it ik) A substance that changes the speed of a reaction without itself undergoing a permanent change

EXAMPLE Manganese dioxide in the preparation of oxygen

**chemical change** One in which the composition of a substance has changed. It involves an alteration in physical and chemical properties

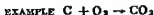
**colloid** (kol oid) A substance the particles of which are intermediate in size between coarse suspensions and molecules

EXAMPLE Gelatin (a colloid) has particles or films smaller than clay (a suspension) and yet larger than the molecules of salt dissolved in water

**combustion** A rapid chemical action producing light and heat

EXAMPLE Burning of wood

**compound** A combination of two or more elements



**covalence** (kō-vā' lēns) The chemical binding of atoms through sharing of electrons

**destructive distillation** Process of decomposing complex organic compounds by heat in the absence of air, and condensing the vapor of the liquid products

EXAMPLE Heating soft coal

**dialysis** (dī al ī sis) The separation of a crystalloid from a colloid by use of a membrane

**diffu'sion** Process by which a substance in solution distributes itself uniformly throughout the solvent

**distilla'tion** The separation of a liquid from a mixture by boiling and condensing the vapor

EXAMPLE In the distillation of impure water, the pure water is separated from its impurities

**electrolysis** (e-lek trol ī sis) The decomposition of a substance in a solution by the electric current

EXAMPLE The electrolysis of water to yield hydrogen and oxygen

**electrolyte** (e-lek tro lite) A substance the solution of which conducts the electric current and is decomposed by it

EXAMPLES Hydrochloric acid, sodium hydroxide, sodium chloride

**electron** (e-lek'tron) Particle of negative electricity

**element** One of some one hundred simple substances which are the basis for chemical changes

EXAMPLES Oxygen, hydrogen, sodium, gold and iron are elements

**emul'sion** A suspension of a finely divided liquid in another liquid

**equa'tion** A symbolic representation of a chemical reaction

**fluorescence** Property a body possesses of emitting light while exposed to the action of certain rays

**for'mula** An arrangement of symbols so as to represent the composition, number, and variety of atoms in a molecule. A symbolic representation of a molecule

**gel** (jel) Semisolid condition of a precipitated or coagulated colloid

**halogen** (hal o-jen) This term means salt former and refers to the elements F, Cl, Br, or I

**hemolysis** (he-mol ī sis) The result of water passing into a blood cell thereby causing it to swell and burst

**hydrate** (hī drate) A crystalline substance containing a definite amount of water in combination.

EXAMPLE Plaster of Paris  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$

**hydrocar'bon** A compound which contains hydrogen and carbon only

EXAMPLE Ethylene,  $\text{C}_2\text{H}_4$

*hydrogen ion or pH scale* A means of indicating accurately any degree of acidity or alkalinity.

*hydrolysis* (hi drof i sis) Any chemical reaction of an element or a compound with water

*hydrophilic* A liking for water, a type of colloid

*hyperton'ic* Pertaining to a solution of higher osmotic pressure than another

*hypoton'ic* Pertaining to a solution of lower osmotic pressure than another

*hypoxia* An inadequate supply of oxygen for metabolism

*ion* An electrically charged atom or radical in solution The loss or gain of one or more electrons by an atom or group of atoms (radical) produces an ion

EXAMPLE  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$

*isoton'ic* Pertaining to two solutions having the same osmotic pressure

EXAMPLE Physiological saline solution is isotonic to the blood

*isotopes* Atoms of an element which differ only in mass All isotopes of a given element have the same atomic number

*kindling temperature* The lowest temperature at which a substance ignites

EXAMPLE The kindling temperature of phosphorus is  $37^\circ \text{C}$

*metal* A base forming substance An element which loses electrons during chemical changes

EXAMPLES Na, Ca, Mg

*mole* A gram formula weight of a substance

EXAMPLE One mole of  $\text{SO}_2$  is 64 grams

*molecule* (mol'e-kule) The smallest particle of a substance that can exist and still retain the properties of that substance

EXAMPLES  $\text{O}_2$ ,  $\text{H}_2\text{O}$

*neutralization* The combination of the hydrogen ions of an acid and the hydroxyl ions of a base to form undissociated water

EXAMPLE  $\text{Na}^+\text{OH}^- + \text{H}^+\text{Cl}^- \rightarrow \text{Na}^+\text{Cl}^- + \text{H}_2\text{O}$

*neutron* A close union of proton and electron, which has no electrical charge

*nonmetal* An acid forming substance An element which gains electrons during chemical changes

EXAMPLES Cl, S

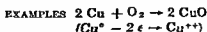
*nonpolar compound.* A compound in which the centers of positive and negative charge coincide

*normal salt* The compound formed when all of the hydrogen of an acid is replaced by a metal

EXAMPLE  $\text{Na}_2\text{CO}_3$

*osmosis* (os mo'sis) The passage of a liquid through a membrane

*oxidation* The process by which a substance combines with oxygen, more generally oxidation involves a change from a lower to a higher positive valence



*oxide* (oks'ide) A compound consisting of oxygen and one other element



*peptize* To disperse an insoluble material into particles of colloidal size

EXAMPLE Pepsin changes protein to peptones

*photosynthesis* (fo to sin'the sis) A synthetic process by which plants manufacture carbohydrates

*plasmolysis* (plaz mol i sis) The result of the passing of water out of a cell, thereby causing the cell to shrink, also called crenation

*polar compound* Compounds in which the centers of positive and negative charge are separated

*proton* A fundamental particle of positive electricity

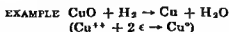
*radical* A group of elements acting as a unit



*radioactive* Pertaining to any substance that emits radiations through spontaneous transmutation

EXAMPLE Radium

*reduction* The process of taking oxygen from a compound more generally a change from a higher to a lower positive valence



*salt* A compound consisting of a positive ion other than hydrogen and a negative ion other than hydroxyl (Salts may be formed in several ways, see text)



*saturated solution* One which contains all the solute that can normally be dissolved at that temperature

*semipermeable* (per me a ble) Pertaining to a membrane which will allow certain substances but not others, to pass through it

*solute* (so lute') The dissolved substance in any solution

*solution* (so lū'shun) A molecular or ionic dispersion

*sol vent* The substance in which anything is dissolved

*specific gravity* The ratio of the weight of one cubic centimeter of a substance to the weight of one ml. of water

EXAMPLE Sp Gr of urine is about 1.02

*specific heat* The number of calories absorbed or given up when one gram of a substance changes its temperature  $1^{\circ}\text{C}$

EXAMPLE Sp Ht of water is 1

*spontaneous combustion* Ignition without the external application of heat

EXAMPLE Spontaneous combustion of coal dust.

*suspensoids* The suspended particles

EXAMPLE Particles in river water

*symbol* An abbreviation for an element

EXAMPLES H for hydrogen Cu for copper

*synthesis* (sin the sis) The union of elements to produce compounds

EXAMPLE  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

*ternary acid* (ter na re) Inorganic acids containing hydrogen and two other elements

EXAMPLES  $\text{H}_2\text{SO}_4$   $\text{HNO}_3$

*valence* (va'lens) 1 The number indicating how many atoms of hydrogen can unite with one atom of another element 2 The number indicating how many electrons an element or radical has gained, lost, or shared through chemical action

EXAMPLE In  $\text{H}_2\text{SO}_4$  the H has a valence of 1 and the  $\text{SO}_4$  a valence of 2

*x rays* Radiations produced by electrons from the cathode striking a target

## PART II

# ORGANIC CHEMISTRY

### THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES

Replacing diseased arteries with synthetic materials is a major triumph of surgery. This one is made of "Teflon," a fluorocarbon. Courtesy, DuPont Magazine, Copyright, 1958, E. I. du Pont de Nemours and Company.





## INTRODUCTORY NOTES

### TO THE INSTRUCTOR

In this division of chemistry, we are to study that large class of compounds which contains the element carbon. It will become an interesting and fascinating study for the student nurse when it is realized that life with all its mysteries dwells permanently among carbon compounds. Those facts, laws, and theories developed in the previous chapters will govern the formation and behavior of most organic compounds. Just as there are oxides, acids, bases, and salts in inorganic chemistry, so there are similar compounds in organic chemistry, but with the main difference that the carbon compounds are weakly electrical in nature. This is largely due to the fact that the carbon atom never exists as an ion in solution, but rather shares its electrons with carbon atoms or atoms of other elements.

The discussion starts with the compounds of hydrogen and carbon, and then it branches to the study of substitution products or derivatives, which are considered as compounds formed by replacing one or more hydrogen atoms in the hydrocarbon molecule by radicals which have characteristic properties. Some of the most frequently substituted radicals which impart new properties are the alcohol group ( $-\text{OH}$ ), and the aldehyde group ( $-\text{CHO}$ ), the ketone group ( $=\text{CO}$ ), the acid group ( $-\text{COOH}$ ), and the amino group ( $-\text{NH}_2$ ).

Since organic chemistry is the chemistry of most articles of everyday life, such as food, clothing, medicines, dyes, perfumes, and flavors, this study in addition to its fascination and interest will be the background for an intelligent interpretation of the chemical changes constantly occurring in the human body (Part III).

## OBJECTIVES

### I. FACTS AND PRINCIPLES

- (a) To learn that the properties of carbon make possible some 500,000 carbon compounds
- (b) To know that organic compounds may be divided into classes showing similarity in composition and properties
- (c) To learn that the principles governing the formation and behavior of *inorganic compounds apply as well to organic compounds*
- (d) To learn that the classification and properties of organic compounds depend largely upon the presence of characteristic groupings in the molecule
- (e) To predict from the formula how an organic compound might behave, and to some extent the possibility of its use
- (f) To become acquainted with the uses of a variety of important carbon compounds

### II. ATTITUDES

- (a) To develop an appreciation of the work of the chemist in producing many valuable substances from plants and animals
- (b) To realize that, in all problems of the future, chemistry with its background of allied sciences is the one science capable of solving many of life's problems
- (c) To realize that to chemical research we owe much for our health and happiness
- (d) To realize that an understanding of organic chemistry is fundamental to the appreciation of many practical human interests whether domestic or industrial
- (e) To realize that organic chemistry is worthy of study from the cultural as well as the scientific standpoint

## CHAPTER XII

# SOME GENERAL FACTS. THE HYDROCARBONS

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### CHAPTER OUTLINE

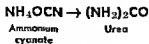
- |   |   |
|---|---|
| I INTRODUCTION  | (f) Sources and properties of the ethylene series of hydrocarbons |
| (a) The origin and importance of organic chemistry      | (g) The acetylene series of hydrocarbons                          |
| (b) Differences between inorganic and organic compounds | (h) Three typical aliphatic hydrocarbons                          |
| (c) Sources of organic compounds                        | (i) The cycloparaffins Cyclopropane                               |
| II STRUCTURAL THEORY OF ORGANIC COMPOUNDS               | (j) The aromatic hydrocarbons Benzene                             |
| (a) The carbon atom                                     |   |
| (b) Classes of organic compounds                        |   |
| III THE HYDROCARBONS                                    | IV HALOGEN DERIVATIVES  |
| (a) Classification                                      | (a) Some common halogen substitution products                     |
| (b) The methane series                                  |   |
| (c) The hydrocarbon radicals                            | V PETROLEUM   |
| (d) Sources and properties of the paraffin hydrocarbons | (a) Composition of petroleum                                      |
| (e) The ethylene series of hydrocarbons                 | (b) Refining of petroleum   |
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## I. INTRODUCTION

### The Origin and Importance of Organic Chemistry:

About the beginning of the nineteenth century chemists were becoming increasingly aware of a rather large number of compounds which were associated with plants and animals. For a number of years the general conclusion prevailed that these compounds could be synthesized only through life processes. This led to the *vital force theory*. Inasmuch as this theory rested on the assumption that the living organs and tissues in plants and animals produced these substances, they came to be known as organic compounds, and the branch of chemistry which dealt with them was termed organic chemistry.

In 1828 a German chemist, Friedrich Wohler, succeeded in preparing urea by heating and evaporating a solution of ammonium cyanate



Urea is a product of body metabolism, and therefore a typical organic compound, ammonium cyanate, however, was known as an inorganic compound. Wohler's synthesis of urea was an important achievement in the history of chemistry because it marked the first time that a scientist had knowingly prepared an organic compound from an inorganic one. Since the time of Wohler's work chemists have synthesized in their laboratories many compounds which are also produced in nature in the course of life processes. Hence the older concept of vital force as essential has been disproved. Since carbon is a necessary element in all organic compounds, organic chemistry is today rather simply defined as *the chemistry of the compounds of carbon*.

Actually a few compounds of carbon, because of their properties and relationships, are included in inorganic chemistry. These are for the most part the oxides of carbon and the carbonates. A number of the latter are found in nature as minerals. To repeat, then, in its broadest sense, organic chemistry is the branch of chemistry which deals with the compounds of carbon.

The importance of organic chemistry is shown in the daily use of many products which are in themselves of organic composition or which have required the use of organic substances in the course of their manufacture. Of particular importance is the development of new medicinal compounds and improvement in purity of those drugs which occur in nature. The majority of dyes and perfumes and the fabrics used for clothing and furnishings are of organic composition. Fuels like gasoline, natural gas, and fuel oil are mixtures of organic compounds.

Equally as important, however, is that one must appreciate the fact that the major classes of foodstuffs, namely, fats, carbohydrates, and proteins, are organic compounds. This is true also of the vitamins. A primary reason for devoting some time to a study of the fundamentals of organic chemistry is to make it possible for the student to understand and better appreciate the chemical reactions which take place in the body. The processes of digestion and metabolism are chemical changes which involve the use and the production of compounds of carbon.

### **Differences between Inorganic and Organic Compounds:**

In addition to acquainting the student with the underlying laws and theories of chemistry the preceding chapters in this textbook have dealt with a few of the more important elements and their



Fig. 1—A Boy Made the First Aniline Dye. William H. Perkins in 1856, at the age of 17, while working with coal tar in his laboratory under the eaves of his English home, made the first synthetic dye "mauve." He was attempting to make quinine, but instead by accident made a beautiful violet-purple dye. What was the outcome of such a discovery? Courtesy, Parke, Davis & Co., N. Y. C.

inorganic compounds. Since we are now to give some attention to organic compounds it is appropriate at this point to note certain significant differences between the organic and inorganic types.

**ABUNDANCY:** A recent estimate places the number of inorganic compounds on record as close to one-half million, and the number of organic compounds as nearing the two million mark. Later we shall learn that carbon atoms share electrons with one another to establish covalent type of linkages. This is a primary reason for the excess of organic compounds over the inorganic ones.

**STABILITY:** In general, organic compounds have lower melting points and boiling points than do inorganic compounds. Also, organic compounds are usually less stable to light and heat than are the inorganic. For this reason, more sensitive organic com-

pounds may be stored in colored glass containers, and kept under refrigeration

**SOLUBILITY** Many inorganic compounds are soluble in water. Very few are appreciably soluble in organic solvents such as ether, benzene, and carbon tetrachloride. In contrast, numerous organic compounds are not soluble in water, but are readily soluble in organic solvents. However, these statements about solubility have numerous exceptions, and are therefore to be regarded as broad generalizations.

**RATE OF REACTION** Inorganic reactions tend to be very rapid, in many cases seemingly instantaneous, while organic reactions as a rule are slow. This is due to the fact that many inorganic compounds are ionic structures while organic compounds are covalent. Ionic reactions are rapid, in contrast, covalent molecules usually react rather slowly. To illustrate, the addition of a solution of silver nitrate to one of sodium chloride gives an immediate precipitation of silver chloride. On the other hand the reaction of an alcohol with an organic acid takes place so slowly that often one must wait several hours before any considerable amount of product is obtained.

**COMBUSTIBILITY** Many organic compounds are combustible, and the vapors of some, when mixed with air, give explosive mixtures. Some organic compounds when heated will first char, indicating the presence of carbon. Very few inorganic compounds are combustible.

**NUMBER OF ELEMENTS** In a study of inorganic compounds many chemical elements are considered. In contrast, the organic compounds are built up from relatively few elements. Carbon and hydrogen alone account for thousands of compounds. Thousands more are restricted to carbon, hydrogen, and oxygen, these include the alcohols, ethers, carboxylic acids, carbohydrates, fats and others. With possibly a few exceptions, carbon, hydrogen, oxygen, nitrogen, the halogens, sulfur and phosphorus are the only elements that enter into the organic compounds to be studied in this course.

**COMPLEXITY OF STRUCTURE** For the most part the organic compounds are much more complex in structure than are the inorganic ones. There is usually a greater number of atoms in organic molecules, and often a given number of atoms can be arranged differently to give distinctly different compounds. Thus  $C_2H_6O$  is the molecular formula for a certain ether and also the

molecular formula for one of the alcohols. This feature of organic chemistry, wherein two or more different compounds have the same molecular formula, is called *isomerism*. Notice that the molecular formula shows only the kind and number of atoms in the molecule, and not necessarily how they are arranged.

### Sources of Organic Compounds:

From plants and animals we obtain many of our organic compounds such as starches, sugars, fats, proteins, alkaloids, and dyes. Many of these compounds, either through natural processes or laboratory synthesis, may be converted into other valuable organic substances. Illustrative is the fermentation of sugar to produce ethyl alcohol. The alcohol so produced may in turn be used to prepare a variety of useful compounds such as the anesthetics, ether and ethylene.

Other organic compounds are obtained from coal, wood, petroleum oil, and bones by *destructive distillation*, a process of decomposing a substance by heating in the absence of air. Coal tar, coal gas, and ammonia from coal, as well as acetic acid, wood alcohol, and acetone from wood, are formed through destructive distillation.

More recently, many organic compounds have been made by synthesis from inorganic substances. For example, a synthetic rubber called neoprene is prepared indirectly from coke, lime, and other substances.

This brief discussion should make it clear that nature and the scientist in his laboratory work in conjunction to provide man with a wide variety of organic compounds.

### SELF-TESTING QUESTIONS

- 1 What is the origin and the present meaning of the term "organic chemistry"?
- 2 What discovery led to the preparation of organic compounds?
- 3 In what way does a knowledge of organic chemistry contribute to (a) industry, and (b) biochemistry?
- 4 Name and explain, giving examples, a number of ways in which organic and inorganic compounds differ.
- 5 What are the two general sources of organic compounds?
- 6 What compounds used in the hospital may be obtained from sugar?
- 7 What is destructive distillation? What products may be obtained by this process?
- 8 Why does carbon form so many more compounds than do other elements?

## II. STRUCTURAL THEORY OF ORGANIC COMPOUNDS

### The Carbon Atom:

Chains and rings of carbon atoms become the framework for organic molecules. Carbon is invariably tetravalent, and this fundamental point must be kept in mind at all times when writing structural formulas.

The structure of the carbon atom shows four valence electrons, that is, four electrons in the outer shell. When a carbon atom

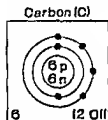


Fig 2—Carbon with its four valence electrons.

shares its electrons with other carbon atoms, or with atoms of other elements, forces of covalence are established.

The compound methane,  $\text{CH}_4$ , has the following structure. In the methane molecule the carbon atom is sharing its four valence electrons with the hydrogen atoms, each of which in turn shares its one electron with the carbon. In this way four covalent forces are established between the carbon and the hydrogens. Outer electron shells thus become complete, the carbon atom having eight electrons around it, and each hydrogen two, but this is possible only by sharing valence electrons as common property.

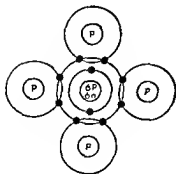


Fig 3—The carbon atom shares with each hydrogen a pair of electrons, one electron from the carbon and one from each hydrogen.



Structures like that for methane are simplified by the use of the short straight line to represent each pair of shared electrons. This gives the structural formula. Notice that the short line, or valence bond, as it is called, is merely a more convenient way of picturing a pair of shared electrons.



Fig 4—Simplified structures for methane. On the left is the electronic structure. On the right the line bond replaces the pair of shared electrons.

Following are the electronic type formulas for ethyl alcohol and methyl ether. Recall in examining these structures that the oxygen



atom has six valence electrons, the carbon atom four, and the hydrogen atom one. Notice too that in each structure each of the carbon atoms has a total of eight outer shell electrons, the oxygen eight, and the hydrogens two. However, this attainment of stable numbers of electrons by the atoms involved is possible only by sharing. Observe that in each of these structures the oxygen atom shares but two of its six original electrons, but by sharing two has a covalence of two.

These structures are simplified to give the more conventional structural formulas.



When one condenses these structural formulas to molecular formulas the result for each is  $\text{C}_2\text{H}_6\text{O}$ . Therefore these two compounds are isomers. *Isomers are compounds which have the same kind and number of atoms in the molecule, but which differ in the arrange*

ment of these atoms in the structure of the molecule. From this it should be apparent that in organic chemistry the molecular formula alone is usually not adequate because it does not show how the atoms are arranged and linked together.

### Classes of Organic Compounds

As has been stated, there are many thousands of organic compounds, and the task of studying them individually would be an impossible one. Fortunately, based upon structural similarities, it is possible to classify organic substances. Some of the more important and fundamental classes and types which are to be considered are given in the table.

IMPORTANT CLASSES OF ORGANIC COMPOUNDS

Hydrocarbons Alcohols Aldehydes Ketones	Carboxylic acids Ethers Esters Amines	Carbohydrates Fats Proteins
--	--	-----------------------------------

The carbohydrates, fats, and proteins become of particular importance, and for this reason an entire chapter will be devoted to each. Inasmuch as all organic compounds can be considered as derived from the hydrocarbons, we shall study the hydrocarbons in this introductory chapter.

### SELF-TESTING QUESTIONS

- 9 What property of the carbon atom makes possible the formation of so many compounds of carbon?
- 10 What are isomers? Why must the organic chemist use structural formulas?
- 11 On what basis is it possible to classify organic compounds?
- 12 What does the single bond in structural formulas stand for?

## III THE HYDROCARBONS

### Classification

Since carbon has a valence of four it would seem that there would be but one hydrocarbon, namely,  $\text{CH}_4$ . However, we must note that carbon atoms can share electrons and in this way attach themselves in chains and rings. Hundreds of hydrocarbons are known, and from structural considerations many thousands become

possible of existence and preparation. *Hydrocarbons are organic compounds which are built up from carbon and hydrogen as the only elements.* This statement about the composition of hydrocarbons should be kept in mind by the beginner in his approach to organic chemistry. In the study of hydrocarbons as well as other classes of organic compounds, emphasis will be placed on class properties. Based on structure, the hydrocarbons can be classified as shown in the accompanying table. The name and formula for the first member of each series is included in the table.

### A CLASSIFICATION OF HYDROCARBONS

#### *Aliphatic Hydrocarbons* (Open Chain Structures)

<p>Methane series (paraffins) Alkanes</p> <p><math>\text{CH}_4</math></p> <pre>       H         H — C — H               H           </pre> <p>Methane</p>	<p>Ethylene series (olefins) Alkenes</p> <p><math>\text{C}_2\text{H}_4</math></p> <pre>       H   H             H — C = C — H           </pre> <p>Ethylene</p>	<p>Acetylene series Alkynes</p> <p><math>\text{C}_2\text{H}_2</math></p> <p><math>\text{H} - \text{C} \equiv \text{C} - \text{H}</math></p> <p>Acetylene</p>
---	--	--

#### *Cyclic Hydrocarbons* (Ring Structures)

<p>Cycloparaffins</p> <p><math>\text{C}_3\text{H}_6</math></p> <pre>       H       H                 H — C ——— C — H       \       /        C       /       \       H       H           </pre> <p>Cyclopropane</p>	<p>Aromatics</p> <p><math>\text{C}_6\text{H}_6</math></p> <pre>           H                       C         /  \       H—C    C—H                      H—C    C—H         \  /           C                       H           </pre> <p>Benzene</p>
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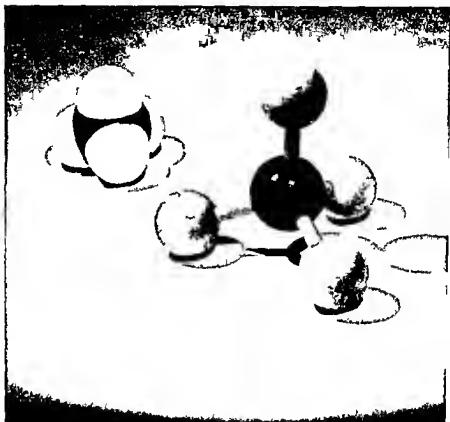


Fig 5—Models of the Methane Molecule. The model on the right is a ball and stick type while the one on the left is a space model. What is the nature of covalence? Courtesy Tobias Studio Akron Ohio

### The Methane Series

The table which follows gives names and other data for the first several members in the methane or paraffin series of hydrocarbons. Hydrocarbons of this series are called *alkanes* in systematic naming.

All members of this series must conform to the general or type formula  $C_nH_{2n+2}$  where  $n$  is the number of carbon atoms in the molecule. Thus if a certain hydrocarbon contains seven carbon atoms then it must also contain  $(2 \times 7) + 2$  or 16 hydrogen atoms in order to be a member of the methane series. A hydrocarbon of molecular formula  $C_8H_{16}$  could not be classified as an alkane.

The paraffin hydrocarbons represent a typical *homologous series*.

## THE METHANE SERIES

Name	Molecular Formula	Possible Structures
Methane	$\text{CH}_4$	1
Ethane	$\text{C}_2\text{H}_6$	1
Propane	$\text{C}_3\text{H}_8$	1
Butanes	$\text{C}_4\text{H}_{10}$	2
Pentanes	$\text{C}_5\text{H}_{12}$	3
Hexanes	$\text{C}_6\text{H}_{14}$	5
etc		

of organic compounds. In any homologous series consecutive members differ by the amount of one carbon and two hydrogens, that is, by the unit  $-\text{CH}_2-$ . It is customary to refer to members of such a series as *homologues*. We shall find that homology is the nature of other classes of organic compounds.

The listing given in the table is by no means complete for this series, it continues with an increasing number of carbon atoms in the molecules. Paraffin hydrocarbons having nearly one hundred carbon atoms in the molecule are known.

## Structures of the Methane Hydrocarbons. Isomerism.

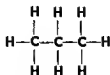
The table points out that there is one possible methane, one ethane, one propane, two butanes, and three pentanes. The two butanes, molecular formula  $\text{C}_4\text{H}_{10}$ , must have different structures and hence are isomers. The same situation exists for the three pentanes. Structural formulas follow.



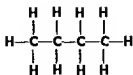
Methane



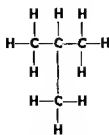
Ethane



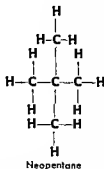
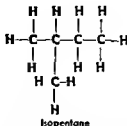
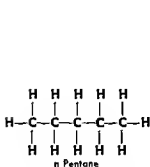
Propane



Normal butane



Isobutane



Examine carefully the structures for the two butanes and be certain that you understand wherein they differ. Notice, for example, that in normal butane the carbon atoms are in one continuous chain, while in isobutane the longest continuous chain of carbons is three\*. Hydrocarbons which have all of the carbon atoms in the molecule in one continuous chain are indicated in naming as *normal*, usually abbreviated as *n*-. Both of the butanes are known, and they have different physical and, to some extent, different chemical properties. In a similar manner study the structures for the three isomeric pentanes.

In the structures for the paraffin hydrocarbons it is to be noted that all bonds connecting carbons are angle bonds, and that each bond stands for a pair of shared electrons. Hydrocarbons of this type are said to be *saturated*. We shall find that this is in contrast to the hydrocarbons which make up the ethylene and the acetylene series. *The alkanes are saturated hydrocarbons*.

As the number of carbon atoms in the molecule increases, the number of isomers possible increases rapidly. Theoretically there are seventy five isomeric decanes, all, however, have the molecular formula  $\text{C}_{10}\text{H}_{22}$ .

### The Hydrocarbon Radicals\*

In the study of inorganic compounds it was learned that there are certain rather stable groups of atoms called radicals, for example the sulfate radical,  $\text{SO}_4$ , and the ammonium radical,  $\text{NH}_4$ . Similarly radicals exist in organic structures, and inasmuch as some of these are comprised of only carbon and hydrogen, and are important in naming compounds and in writing formulas and equations, they are now considered. Names and structures for a few of the simpler,

\*Models are helpful in learning to understand isomerism.

but nonetheless very important, ones are listed in the table. Notice that the radical is a part of a molecule, some atom or group must be attached to the radical to make a complete molecule. Hydrocarbon radicals of this type are known as *alkyl groups*.

## SOME HYDROCARBON RADICALS

Radical Name	Structure	Condensed Structure
Methyl	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}- \\   \\ \text{H} \end{array}$	$\text{CH}_3-$
Ethyl	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	$\text{C}_2\text{H}_5-$
n Propyl	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}- \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_2-$
Isopropyl	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \quad \text{H} \end{array}$	$(\text{CH}_3)_2\text{CH}-$
n Butyl	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}- \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$

Notice that there are two different propyl radicals, but only one propane. If one attaches a hydrogen atom to either of the propyl radicals the result is the same compound, namely, propane. However, if some atom other than hydrogen, or some group of atoms, is attached then different (isomeric) compounds result. There are, for example, two different propyl alcohols. One is called normal propyl alcohol and the other, its isomer, is isopropyl alcohol.

In addition to the n butyl radical there are three other butyl radicals. These are named isobutyl, secondary butyl, and tertiary butyl.

## Sources and Properties of the Paraffin Hydrocarbons:

The hydrocarbons of the methane series are obtained largely from natural gas and petroleum. The former is essentially methane, often over 80 per cent, with relatively small quantities of other hydrocarbons.

Petroleum is an exceedingly complex mixture of compounds, predominantly liquid hydrocarbons. Quantities of gaseous hydrocarbons are dissolved in the liquids, and dissolved solids are also present. By the process of *fractional distillation* it is possible to separate petroleum into fractions which consist of mixtures of compounds having definite boiling point ranges. Gasoline and kerosene are typical fractions from petroleum oil.

It is also a practice to convert some of the hydrocarbons which have the higher molecular weights into simpler hydrocarbons of smaller molecular weight by processes called "cracking." This requires the use of catalysts and usually elevated temperatures and pressures. The smaller molecular weight molecules obtained in this way are more volatile, and some are suitable for gasoline mixtures. Also, certain types of simple hydrocarbon molecules can be made to join together and give larger molecules. This is called *polymerization*. The vast petroleum industry can today by fractional distillation, cracking, and polymerization provide from crude petroleum oil the many industrially important hydrocarbon mixtures of which the various gasolines, fuel gases, and fuel oils are of outstanding importance.

The lower members of the alkane series of hydrocarbons are gases, beginning with those which have five carbon atoms, and extending to some having as many as twenty five carbon atoms in the molecule, they are liquids. Higher members are solids, paraffin wax, for example, is a mixture of solid hydrocarbons. All hydrocarbons are insoluble in water.

In general, the paraffin hydrocarbons are rather inert chemically. This is due in part to their saturated character. Thus, they may be treated with aqueous oxidizers, with strong alkalis, and even with concentrated mineral acids at room temperature without any chemical activity. Such lack of reactivity is an important property of the saturated hydrocarbons. The word paraffin in its derivation means "little affinity."

There are several characteristic chemical reactions of the alkanes, and two of these are to be considered here. One of these is combustion.

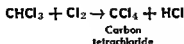
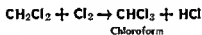
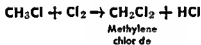
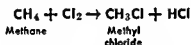


tion, or, as it is sometimes termed, high temperature oxidation. The paraffin hydrocarbons, and all other types of hydrocarbons for that matter, are highly combustible, they burn in oxygen, or in air which supplies the oxygen, to give carbon dioxide and water as the products of complete combustion. During this process, energy, predominantly in the form of heat, is liberated. This liberation of energy accounts for the widespread industrial and domestic uses of hydrocarbons and hydrocarbon mixtures as fuels.

An equation which expresses the combustion of ethane follows



Another type of reaction which is shown by the methane series of hydrocarbons is called *substitution*. This involves the replacement of one or more hydrogen atoms in the hydrocarbon molecule by one or more other atoms or radicals. We shall confine our study of substitution to the use of chlorine and bromine, this can then be called *halogenation*. The equations below illustrate substitution.



Here all four of the hydrogens in the methane molecule have been replaced in a stepwise fashion by chlorine atoms. Notice that each of the reactions of substitution gives two products. The use of the halogens in substitution is confined to chlorine and bromine, iodine is not reactive with hydrocarbons, and fluorine proves to be so highly reactive that the organic structure is broken down. Replacement of hydrogens in hydrocarbons by chlorine and bromine is favored by elevated temperatures and actinic light. Chloroform, carbon tetrachloride, etc., are not prepared commercially according to the reactions just given because, as is shown, a number of substi-

tution products are formed at the same time, and it is not economically feasible to separate them

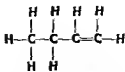
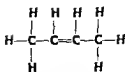
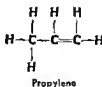
### The Ethylene Series of Hydrocarbons:

The table gives the names and molecular formulas for the first several members in the ethylene series. This series of hydrocarbons is known also as the olefin series, and the members are termed *alkenes*

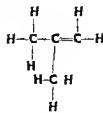
THE ETHYLENE SERIES

Name	Molecular Formula	Number of Structures
Ethylene	$C_2H_4$	1
Propylene	$C_3H_6$	1
Butylenes	$C_4H_8$	3
Amylenes	$C_5H_{10}$	5
Hexylenes etc	$C_6H_{12}$	13

The olefin hydrocarbons are unsaturated, this is indicated in the structure of each olefin by the presence of one double bond between adjoining carbon atoms. The structural formulas which follow illustrate this important characteristic



The three butylenes



The double bond is the symbol employed for four shared electrons, or since electrons are shared in pairs the double bond stands

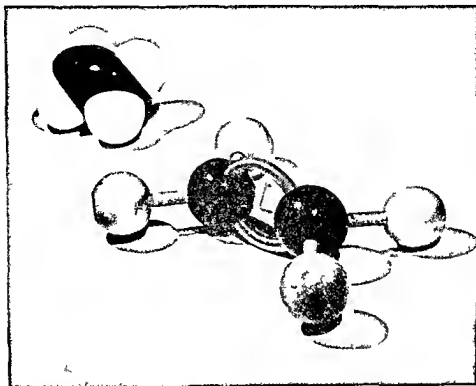


Fig. 6—Models of the Ethylene Molecule. How does the model show the unsaturation found in ethylene? Courtesy Tobias Studio, Akron, Ohio

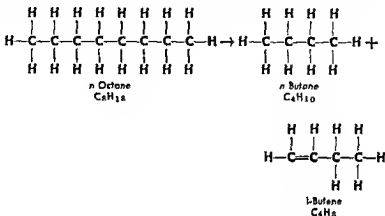
for two pairs of shared electrons. It is not to be considered as a point of structural strength and stability in the molecule; actually the double bond is a center of chemical activity, and the more characteristic chemical reactions of these hydrocarbons involve the point of unsaturation.

In addition to the structures for ethylene and propylene, the structures for the three butylenes are given primarily to point out that the molecular formula  $C_4H_8$  represents three isomeric unsaturated hydrocarbons. Observe also that the olefin series is a homologous series of hydrocarbons. The general formula for this series to which all members must conform is  $C_nH_{2n}$ .

### Sources and Properties of the Ethylene Series of Hydrocarbons

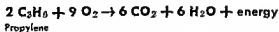
Unlike the paraffin hydrocarbons, the alkenes occur in nature only in traces; for example, very small quantities of ethylene are found in natural gas. However, large quantities of the olefins can

be made commercially by cracking the paraffin hydrocarbons (See page 266) The equation which follows gives a somewhat simplified version of how a butylene (1 butene) might be formed by cracking normal octane

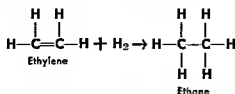


The olefins of lower molecular weight are gases. Beginning with those of five carbon atoms they become liquids. Like all hydrocarbons, the alkenes are insoluble in water.

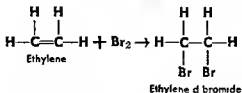
The members of the ethylene series, principally because of the double bond which gives them unsaturation, are far more reactive than the paraffins. The olefins are combustible and, like all other hydrocarbons, if the supply of oxygen is adequate, they burn to give carbon dioxide and water with liberation of energy, largely as heat. By way of illustration, propylene gas burns according to the following equation:



The most typical chemical reaction of the alkenes is called addition. Because of unsaturation it is possible for these hydrocarbons to add such substances as hydrogen, chlorine, and bromine. In the course of the addition the double bond gives way to a single bond, and hence the unsaturation disappears and the product of the reaction is saturated. Ethylene and its homologues, under proper conditions which include the use of a catalyst, add on hydrogen.



The addition of bromine to ethylene proceeds as follows



The addition of chlorine and bromine to unsaturated hydrocarbons is favored by low temperature and the absence of light. Notice that in the addition type of reaction only one product is formed. The student should at this point contrast substitution with addition, turning back, if necessary, to the discussion of the reaction of paraffin hydrocarbons with bromine and chlorine.

In conclusion, another typical reaction of olefinic hydrocarbons is *polymerization*. Because of unsaturation it becomes possible for molecules to add to one another and build up hydrocarbons of high molecular weight. One of the newer polymeric substances which is finding a variety of uses is polyethylene or polythene, prepared from ethylene. Polypropylene is a similar polymer.

### The Acetylene Series of Hydrocarbons

The hydrocarbons of this series, like those of the ethylene series, are unsaturated. However, the degree of unsaturation is higher, and it is represented by a triple bond between adjacent carbons. The triple bond becomes a simple way of representing three pairs of shared electrons. The data of the accompanying table and the

THE ACETYLENE SERIES

Name	Molecular Formula
Acetylene	$\text{C}_2\text{H}_2$
Methylacetylene	$\text{C}_3\text{H}_4$
Dimethylacetylene	$\text{C}_4\text{H}_6$
Ethylacetylene	$\text{C}_4\text{H}_6$
	} isomers

structures given illustrate a number of the acetylenic hydrocarbons. All conform to the type formula  $C_nH_{2n-2}$ .

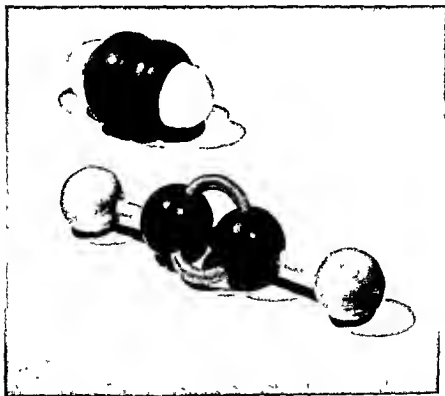
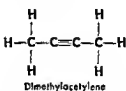
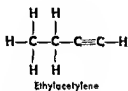
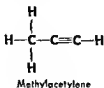
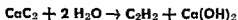


Fig 7—Models of the Acetylene Molecule. How many atoms of hydrogen can be added to one molecule of acetylene? Courtesy, Tobras Studio, Akron, Ohio

In scientific nomenclature the hydrocarbons of the acetylene series are called *alkynes*. By far the most important hydrocarbon of this series is acetylene itself. Acetylene does not occur in nature, but it can be made very easily from calcium carbide and water at room conditions.



Acetylene gas with air forms highly explosive mixtures, and care must be used in preparing and using this hydrocarbon.

The acetylenic hydrocarbons, in a general way, exhibit the same reactions as the olefins, this is to be expected because both types are unsaturated. Inasmuch as the degree of unsaturation is higher in the acetylenes it is necessary for them to add on greater amounts of hydrogen, chlorine, etc., before becoming saturated. The ethylene molecule, as we have seen, becomes saturated by adding on one molecule (two atoms) of bromine. To saturate the acetylene molecule two molecules of bromine are required.

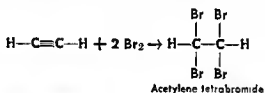


Fig. 8—The Greatest Use of Acetylene. The oxyacetylene flame, produced by burning acetylene in pure oxygen, is a source of intense heat ( $3300 \pm ^\circ\text{C}$ ), and is used in welding, cutting, and melting metals or their alloys. What elementary substance, previously studied, burns in oxygen to provide a similar high temperature flame? Courtesy, Linde Co.

By self addition, or addition to similar molecules, acetylenic hydrocarbons form higher molecular weight products. Acetylene, for example, is a starting material for the preparation of neoprene, a high molecular weight polymer which has rubber-like properties.

### Three Typical Aliphatic Hydrocarbons:

Inasmuch as methane, ethylene, and acetylene are very important and also representative members of their respective series, some further facts about them are included in the table which follows

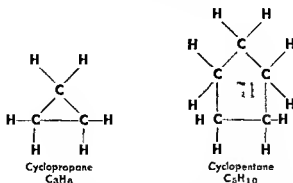
THREE IMPORTANT ALIPHATIC HYDROCARBONS

Hydrocarbon	Physical State	Properties and Uses
Methane $\text{CH}_4$	Gas	Combustible. Known also as marsh gas and fire damp. Occurs in natural gas. Valuable as a fuel and for the preparation of gas black (lamp black). A constituent of intestinal gases from decomposition of food residues.
Ethylene $\text{CH}_2=\text{CH}_2$	Gas	Combustible. Mixed with oxygen, ethylene is a useful anesthetic. Mixed with air, in low concentration, ethylene is used to change the color of green fruits, for example, citrus fruits, to the color of ripe fruit.
Acetylene $\text{CH}\equiv\text{CH}$	Gas	Highly explosive with air. When properly burned gives a brilliant white light and intense heat. Used with oxygen in the oxyacetylene torch. Raw material for synthesis of many organic compounds.

### The Cycloparaffins. Cyclopropane:

The cycloparaffins are ring structures, and inasmuch as the members of the series are saturated their chemistry is in many respects similar to that of the aliphatic paraffins. The structures for two typical members of this series are presented here.





Cyclopropane, a colorless gas, is of particular importance because of its use as an inhalation anesthetic. When thus employed it is mixed with oxygen. The chief disadvantage in its use as an anesthetic is its explosive character. It has the advantage of being nonirritating, and recovery is rapid with no ill after effects.

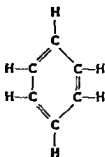


Fig. 9—An Anesthetic. Cyclopropane ( $\text{C}_3\text{H}_6$ ) or trimethylene made its first clinical appearance in 1933 at the University of Wisconsin.

Before dismissing the cyclic aliphatic hydrocarbons it is to be pointed out that there are also cyclo olefins. These are cyclic hydrocarbons in which a double bond appears between adjacent carbon atoms. Cyclohexene,  $\text{C}_6\text{H}_{10}$ , is one of the best known hydrocarbons of this type.

### The Aromatic Hydrocarbons Benzene

All of the aromatic hydrocarbons and their many derivatives exhibit a type of structure known as the benzene or aromatic ring. The simplest and most important hydrocarbon of the aromatic division is benzene.



The aromatic ring, as depicted in the structure of benzene itself, consists of six carbon atoms with single and double bonds placed in alternate positions around the ring. Such an arrangement of bonds makes each carbon tetravalent. The presence of the double bonds implies that considerable unsaturation should exist. However, the unsaturation of the aromatic ring is of an unusual type, and ordinarily the replacement of the hydrogens, which is substitution, is much more readily accomplished than is addition to the double bonds. Later there will be occasion to consider some of the derivatives of benzene, and it will be found that these are the result of replacing one or more of the hydrogens of benzene with other atoms or radicals.

Benzene is a colorless liquid of characteristic odor. One of the most important sources of this hydrocarbon is coal tar, a liquid obtained as a by-product in the preparation of coke by the destructive distillation of soft coal. Benzene has great value as the starting material for the preparation of a large number of synthetic aromatic compounds.

### SELF-TESTING QUESTIONS

- 13 What are the names of the various series of hydrocarbons?
- 14 What is the important structural difference between the saturated and the unsaturated hydrocarbons?
- 15 Why is it impossible for an alkane to form addition products?
- 16 To what series of aliphatic hydrocarbons would  $C_{12}H_{22}$  belong?
- 17 What are homologues? What are isomers? Illustrate.
- 18 What is polymerization? Why cannot the alkanes show this type of reaction?
- 19 In what respects is cyclopropane like propane? How do they differ?
- 20 How is it possible to have five different hydrocarbons, all of formula  $C_6H_{14}$ ? Illustrate by giving suitable formulas.

- 21 What chemical property is characteristic of all hydrocarbons, regardless of structure?
- 22 How does the substitution type of reaction differ from the addition type?
- 23 How many products are formed in a substitution reaction? How many are formed in the addition reaction?
- 24 How is acetylene prepared? Write the equation for its combustion
- 25 What is a structural characteristic of all aromatic compounds?
- 26 How does the unsaturation pictured by the benzene ring compare with the unsaturation of ethylene and other olefins?

#### IV. HALOGEN DERIVATIVES

##### Some Common Halogen Substitution Products:

There are a number of halogen derivatives of the hydrocarbons which because of their uses merit consideration at this point. Several have already been mentioned in this chapter in connection with the reactions of the hydrocarbons. The table (page 278) gives the names, structures, and other pertinent data.



Fig 10—A Carbon Tetrachloride Fire Extinguisher



Fig 11—Local or General Anesthesia Ethyl chloride. Used in minor surgery. What is the appearance of the skin when frozen?

The first four compounds in the table can be looked upon as derivatives of the hydrocarbon methane. Ethyl chloride is structurally related to ethane, and trichloroethylene is derived structurally from ethylene.

## SOME HALOGEN DERIVATIVES OF HYDROCARBONS

Name	Structure	Physical State	Uses
Chloroform	$\begin{array}{c} \text{H} \\   \\ \text{Cl}-\text{C}-\text{Cl} \\   \\ \text{Cl} \end{array}$	Colorless liquid	Anesthetic Solvent for fats and oils
Carbon tetrachloride	$\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{C}-\text{Cl} \\   \\ \text{Cl} \end{array}$	Colorless liquid	Solvent for fats and oils Fire extinguisher
Iodoform	$\begin{array}{c} \text{H} \\   \\ \text{I}-\text{C}-\text{I} \\   \\ \text{I} \end{array}$	Yellow solid	Mild antiseptic activity due to slow liberation of iodine
Dichloro difluoromethane (freon)	$\begin{array}{c} \text{F} \\   \\ \text{Cl}-\text{C}-\text{Cl} \\   \\ \text{F} \end{array}$	Gas (easily compressed to liquid)	Refrigerant in household refrigerators and air conditioners
Ethyl chloride	$\begin{array}{cc} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C} & -\text{C}-\text{Cl} \\   &   \\ \text{H} & \text{H} \end{array}$	Gas (easily liquefied)	Local anesthetic rapid evaporation freezes tissue Inhalation anesthetic
Trichloroethylene	$\begin{array}{cc} \text{Cl}-\text{C} & -\text{C}-\text{Cl} \\   &   \\ \text{H} & \text{Cl} \end{array}$	Liquid	Industrial solvent Used in preparations for cleaning clothes rugs etc

## SELF-TESTING QUESTIONS

- 27 Which halogen derivatives of hydrocarbons have use as anesthetics? Which are useful solvents?
- 28 What are the four chlorine substitution products derived from methane?
- 29 How would you make ethylene dichloride from ethylene?
- 30 In what type of fire extinguisher is carbon tetrachloride found?

Note The remainder of this chapter may be omitted when time must be saved

## V. PETROLEUM, A LIQUID SECOND IN IMPORTANCE TO WATER

Whenever organic material decomposes in the presence of air, most of the carbon unites with oxygen to form carbon dioxide,

but in the absence of air, the carbon is left combined with hydrogen to form the hydrocarbons. They furnish the logical starting point for the study of organic compounds. The commercial importance of these hydrocarbons may be appreciated when we learn that they make up such valuable substances as natural gas, gasoline, kerosene, lubricating oils, petroleum jelly, and paraffin.

### Composition of Petroleum:

Most hydrocarbons come from petroleum, which includes both crude oil and natural gas and is found only in porous rocks, usually of sedimentary origin. The porous rocks, such as sand stone, act as reservoirs for gases and liquids. Gas being the lightest tends to accumulate in the top of the reservoir, while the oil which is lighter than water will in time separate and accumulate above the water. Oil and gas are usually found together, but may occur separately. Although petroleum is widely distributed over the world, the largest part (70 per cent) is obtained in the United States (Fig. 12).

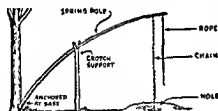
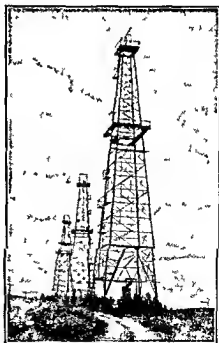


Fig. 12 (Above)—The first wells dug in this country were for salt, and the "spring pole" method employed was adopted in many early oil wells. This consisted of a limber pole, anchored at one end, and passed over a post. Men pulled at the rope at the far end, causing the pole to spring and driving the drilling tools against the bottom of the hole. The method was originated by the Chinese 2,000-odd years ago. Now drilling methods are of two types—Cable Tool (percussion) in hard rock formations and the more commonly used Rotary Method.



(Right)—Giant oil derricks pumping oil, the life blood of the machine age. Petroleum oils are complex mixtures of hydrocarbons, containing sulfur, nitrogen, and oxygen derivatives. Why is it necessary to remove sulfur compounds from gasoline derived from petroleum? Courtesy, H. Armstrong Roberts, Philadelphia.

When this supply becomes exhausted the oil bearing shales of Utah and elsewhere promise to furnish even greater yields of petroleum than now available. Petroleum is of industrial importance chiefly as a source of fuel, of lubricants, and to some extent as a source of solvents. The oil industry has provided the lifeblood of victory in two world wars and has built the United States into a nation on wheels in time of peace.

All petroleum oils are not alike, they contain different kinds of hydrocarbon mixtures, as a result of the decomposition of different varieties of plant life, under different conditions of temperature and pressure. Some oils even point to animal origin. All contain a varying amount of ill smelling sulfur compounds, which make them objectionable for most commercial uses. In buying automobile oil and gasoline we bear continual reference made to oils of a paraffin or of an asphalt base. Pennsylvania oil has a paraffin base and makes a fine grade of lubricating oil. On the other hand, our petroleum oils of the West (California) are mostly of an asphaltum base and are supposed to give an excellent grade of gasoline, but not such good lubricating oils, however, in the light of present refining methods it is difficult to draw much distinction between these two kinds of oils.

## Refining of Petroleum

Some crude oil is used for fuel but the greater part is subjected to *fractional distillation*, a process whereby different portions boiling at different temperatures are collected separately. The separation, as usually carried out, attempts to produce three main products: gasoline, kerosene, and lubricating oils. In some cases the distillation is stopped at a certain temperature so that there will be left

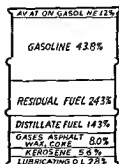


Fig 13—A Drum of Hydrocarbons. Volume of products obtained from a barrel of crude petroleum. To what extent may these percentages vary?

a residue of *asphalt*. At other times the distillation is carried on until nothing is left but *petroleum coke*. Some varieties of petroleum yield, in addition to lubricating oils, a black pitch used in roofing and painting.

The next step in the refining is to remove from the distillates the objectionable materials, such as the foul smelling sulfur compounds and the waxy or tarry substances which oxidize on exposure to air to form gummy products that interfere with burners or carburetors. This is accomplished by agitating the distillate with sulfuric acid, removing the charred material and spent sulfuric acid, carefully neutralizing any remaining acid with a base, and then washing with water to remove all remaining impurities.

The first oil distillate may be refined by being filtered through bone black, which removes the color and improves the odor and taste. In this refined state it is used in medicine to prevent constipation and is commonly called *alholene* or *mineral oil*. From a chemical standpoint the mineral oils have no relation to the animal and vegetable oils in that the mineral oils are not digested or absorbed, but merely act as lubricants.

Since gasoline is the most valuable product of the refining process, the yield of "straight run" gasoline, obtained by distillation of the more volatile hydrocarbons (heptane, octane) has been materially increased (about 50 per cent) by decomposing the heavier molecules of oils into lighter molecules by means of heat and pressure. This *cracking* process produces a large amount of unsaturated aliphatic hydrocarbons, frequently called *olefins*.

The following table throws some light on the physical properties and uses of the commercial products obtained from petroleum:

<i>Name</i>	<i>Specific Gravity</i>	<i>Boiling Point</i>	<i>Uses</i>
Petroleum ether	0.65 to 0.67	35° to 80°	Solvent
Gasoline	0.73 to 0.76	40° to 223°	Fuel
Naphtha	0.66 to 0.80	40° to 225°	Solvent
Kerosene	0.80 to 0.84	175° to 300°	Light, fuel
Lubricating oils	0.86 to 0.95	350° up	Lubrication
Paraffin	0.90 to 0.93	50° to 60° M P.	Candles, wax
Asphalts	0.93 to 1.10	Viscous liquids to 150° M P.	Paving, roofing
Coke			Fuel

## SELF-TESTING QUESTIONS

- 31 What promises to be our greatest natural source of petroleum in the future?
- 32 What is the general difference in composition properties between the oils of Pennsylvania and California?
- 33 What is fractional distillation?
- 34 How do petroleum products differ in their distillates and residues?
- 35 How are impurities removed from gasoline? from oil?
- 36 What is meant by the 'cracking of oils'?

## SUGGESTED ACTIVITIES

## I THOUGHT-PROVOKING QUESTIONS

- 1 How did the work of Wohler aid in our understanding of the normal processes of the body?
- 2 Besides the five general ways mentioned, in what other ways do organic compounds differ from inorganic?
- 3 How has organic chemistry been of aid to the physician?
- 4 What is the meaning of structural, empirical, and molecular formulas?
- 5 Make the structural formula of ethyl alcohol,  $C_2H_5OH$ , and explain why this compound is inactive in solution
- 6 Write graphic formulae showing that carbon may act as a metal or a nonmetal.
- 7 Enumerate all of the reasons for the formation of isomeric compounds
- 8 In addition to the satisfaction of acquiring knowledge what importance is attached to the study of organic chemistry?
- 9 What is the ultimate source of most of the carbon in plant products?
- 10 Considering that fuel gases consist of various hydrocarbons such as methane, ethylene, and acetylene, write equations to show how an inadequate supply of oxygen might account for soot (carbon) deposits on utensils over these burning fuels
- 11 Lubrication of rubber equipment with mineral oil or petroleum jelly tends to dissolve the rubber. What does this solubility show concerning the structure of rubber?

## II VOCABULARY TESTING OF NEW TERMS

organic chemistry	saturated compounds	aliphatic
biological chemistry	substitution products	aromatic
hydrocarbons	unsaturated compounds	heterocyclic
homologous series	isomeric	carbo-cyclic

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Living Organisms Are Chemical Laboratories
- 2 Why Coal Tar Has Become a Valuable By product
- 3 Organic Chemistry in the Service of Medicine
- 4 Some Recent Advances in Medicine Made Possible by Organic Compounds

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 701, 704, 708



# THE ALCOHOLS, ALDEHYDES, KETONES, AND ETHERS

## CHAPTER OUTLINE

- |   |  |
|---|--|
| <b>I THE ALCOHOLS</b><br>(a) Nature of alcohols<br>(b) The series of saturated monohydric alcohols<br>(c) Isomerism<br>(d) Classification of alcohols<br>(e) The oxidation of alcohols<br>(f) Other reactions of alcohols<br>(g) Two important monohydric alcohols<br>(h) Polyhydric alcohols | (b) The oxidation of aldehydes<br>(c) Polymers from aldehydes<br>(d) Two important aldehydes                     |
| <b>II. THE ALDEHYDES</b><br>(a) Nature of aldehydes   | <b>III THE KETONES</b><br>(a) The structure and nature of ketones<br>(b) An important ketone                     |
|   | <b>IV THE ETHERS</b><br>(a) Nature of ethers<br>(b) Preparation and properties of ethyl ether<br>(c) Anesthetics |

## Introduction:

With some understanding of the hydrocarbons we can now consider some series of compounds which contain elements in addition to carbon and hydrogen. We pass from the study of the fundamental hydrocarbons to organic compounds called *derivatives*. These are compounds which are formed by substituting atoms or radicals for an equivalent number of hydrogens in the hydrocarbon.

An element often found in derivatives of hydrocarbons is oxygen. There are three general groups of these compounds of carbon, hydrogen, and oxygen, namely, (1) the alcohols, which may be viewed as first oxidation derivatives of hydrocarbons, (2) the aldehydes and ketones, the second oxidation derivatives, and (3) the carboxylic acids, the third oxidation derivatives. Structurally related to these general groups of oxygen-containing compounds are the ethers and esters, and the carbohydrates and fats.

## I. THE ALCOHOLS

### Nature of Alcohols:

The general public knows two alcohols. These are grain alcohol, which is present in alcoholic beverages, and wood alcohol, a highly poisonous substance. In this chapter we shall find that there are many other alcohols, and that all have a similarity of structure.

The alcohols may be considered as derived from the hydrocarbons, at least structurally, and all of them contain in addition to carbon and hydrogen a third element, oxygen. The characteristic group in which the oxygen appears is the  $-\text{OH}$  structure. When this is found in the inorganic compounds it is customarily called the hydroxyl radical, and the compounds are classified as bases. We have learned that the water soluble bases provide solutions containing hydroxyl ions,  $\text{OH}^-$ . Alcohols, however, are not bases. They are neutral substances and they do not dissociate in water. Therefore somewhat different properties are typical of the  $-\text{OH}$  radical when it is present in organic molecules, and one must think of it as the alcohol group.

Organic chemists frequently use  $\text{R}$  to denote the various hydrocarbon radicals, for example methyl, ethyl, and  $n$  propyl. On this basis one can set up a general formula for the alcohols. This formula is  $\text{R}-\text{OH}$ , and it points out that in its simplest form the alcohol consists of a hydrocarbon radical linked to an alcohol group, i.e., the  $-\text{OH}$  group.

Actually some alcohols contain more than one alcohol group in the molecule. Those containing but one are classified as monohydric, those with two are dihydric, three trihydric, etc. Methyl alcohol,  $\text{CH}_3\text{OH}$ , is a monohydric alcohol, ethylene glycol,  $\text{C}_2\text{H}_4(\text{OH})_2$  is a dihydric alcohol, and glycerol,  $\text{C}_3\text{H}_5(\text{OH})_3$  is trihydric. However, since we are primarily interested in the chemistry of the alcohol group, most of the discussion presented here will be based on the monohydric alcohols.

### The Series of Saturated Monohydric Alcohols

The accompanying table gives the names and formulas for the first several members in the series of monohydric alcohols. All

MONOHYDRIC ALCOHOLS

<i>Name</i>	<i>Formula</i>	<i>Possible Structures</i>
Methyl alcohol	$\text{CH}_3\text{OH}$	1
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	1
Propyl alcohols	$\text{C}_3\text{H}_7\text{OH}$	2
Butyl alcohols	$\text{C}_4\text{H}_9\text{OH}$	4
Amyl alcohols	$\text{C}_5\text{H}_{11}\text{OH}$	8
Hexyl alcohols etc	$\text{C}_6\text{H}_{13}\text{OH}$	17

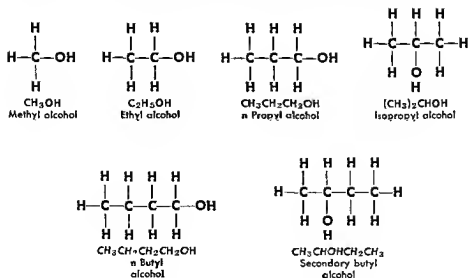
carbon to carbon bonds are single linkages, and therefore these are saturated alcohols

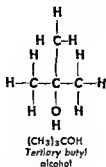
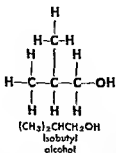
An inspection of this list of alcohols shows that the series is a homologous one, that is, consecutive members differ in formula by the unit  $-\text{CH}_2-$ . Also, using  $n$  to denote the number of carbon atoms in the molecule, the general formula for all members of this series becomes  $\text{C}_n\text{H}_{2n+1}\text{OH}$

Methyl alcohol, ethyl alcohol, and the propyl alcohols are soluble in water in all proportions. Starting with the butyl alcohols the solubility in water falls off rapidly. The lower members of the series are liquids, and possess rather pleasant odors. Higher members are solids. For example, lauryl alcohol,  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ , is a white, water-insoluble solid.

### Isomerism:

Reference to the table shows that beyond ethyl alcohol the type of formula given is not adequate. There are two different propyl alcohols,  $\text{C}_3\text{H}_7\text{OH}$ , and four different butyl alcohols,  $\text{C}_4\text{H}_9\text{OH}$ . Just as was learned in the study of the hydrocarbons, when two or more substances have the same molecular formula one must make use of structural formulas to show how the isomers differ. Following are the expanded and also the condensed structural formulas for the alcohols of this series through the butyl alcohols.





In examining the structures observe how one makes use of the names for the hydrocarbon radicals in naming alcohols

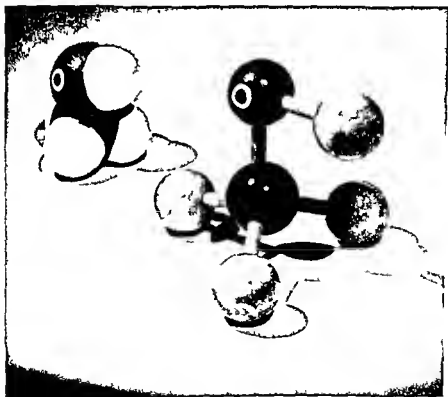


Fig 1—Models of the Methyl Alcohol Molecule The model on the right is the ball and stick type, and the one on the left is a scale model The small white circle identifies the oxygen atom What grouping is distinctive in all alcohols? Courtesy, Tobias Studio, Akron, Ohio

### A Classification of Alcohols:

An important classification of alcohols is made possible on the basis of the position of the alcohol group relative to the remainder of the molecule. In this classification alcohols are designated as primary, secondary, or tertiary. In all primary alcohols, excepting methyl alcohol, the carbon atom to which the alcohol group is joined has attached to it two hydrogen atoms. In the case of methyl alcohol, the simplest of all primary alcohols, the number of attached hydrogens is three. For all secondary alcohols the carbon atom which carries the alcohol group has but one hydrogen directly attached to it, and in the tertiary alcohols the carbon atom carrying the alcohol group has no hydrogens attached. The general formulas for the three classes then become



Primary alcohols



Secondary alcohols



Tertiary alcohols

In all cases, excepting methyl alcohol, R, R' and R'' denote hydrocarbon radicals. Now look back to the section preceding this one and classify each of the eight alcohols as primary, secondary, or tertiary.

This classification becomes important in a study of the alcohols because each type shows in some respects a different chemical behavior from the others. We shall see this now as we turn to a study of the oxidation of alcohols.

### The Oxidation of Alcohols

Alcohols burn to produce carbon dioxide and water when the combustion is a complete one. Ethyl alcohol, for example, burns with a hot, blue flame, and becomes a suitable fuel for alcohol burners and heat lamps.



This equation represents a complete high temperature oxidation.

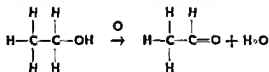
Through the use of aqueous oxidizing agents a number of important classes of organic compounds can be prepared from the alcohols, these are intermediate between the alcohols themselves

and the products of their complete oxidation which we have just seen to be carbon dioxide and water. In this connection the classification as primary, secondary, and tertiary becomes important inasmuch as each type shows a different behavior when oxidized.

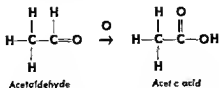
For this kind of oxidation some of the suitable oxidizing agents are potassium permanganate solution, sodium or potassium dichromate solution acidified with sulfuric acid, dilute nitric acid, etc. When ethyl alcohol is treated with neutral potassium permanganate solution the first oxidation product is an aldehyde,  $\text{CH}_3\text{CHO}$ , called acetaldehyde.



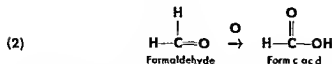
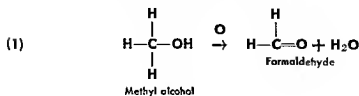
Balanced equations of this type are time consuming to write. In studying the oxidation of alcohols and, on occasion other substances we shall therefore indicate the use of a suitable oxidizing agent like those just mentioned, by writing an O, the symbol for oxygen above the arrow in the equation. In this way the balanced equation which has just been given is greatly simplified.



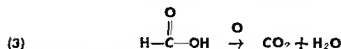
The aldehydes like the primary alcohols from which they are formed, are easily oxidized. Hence, if some provision is not made for promptly removing aldehydes from the presence of the oxidizing agent, they are oxidized to carboxylic acids. Acetaldehyde gives acetic acid.



Methyl alcohol is the simplest of all of the primary alcohols and the stages in its oxidation are as follows

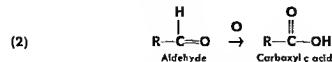
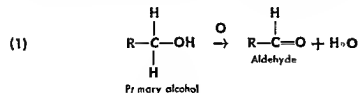


Unlike the other organic acids of its type, formic acid is readily oxidized by aqueous oxidizers to give carbon dioxide and water



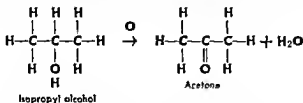
Notice that the number of hydrogens attached directly to the carbon which originally carried the alcohol group decreases from two to none in the oxidation of ethyl alcohol and from three to none (in  $\text{CO}_2$ ) in the oxidation of methyl alcohol

Generalized formulas are helpful in depicting the oxidation of the primary alcohol

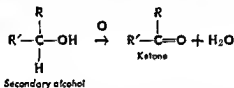


To summarize, the oxidation of a primary alcohol by the use of suitable oxidizing agents produces first the aldehyde. The aldehyde in turn is readily oxidized to the carboxylic acid. In the case of formic acid the oxidation may continue to give carbon dioxide and water. The homologues of formic acid are sufficiently resistant to oxidation to be unaffected. Also, in the study of the behavior of primary alcohols with aqueous oxidizers two new types of organic compounds have been met with, namely, the aldehyde and the carboxylic acid.

The oxidation of secondary alcohols with aqueous oxidizers follows a different course from primary alcohols. The simplest secondary alcohol is isopropyl alcohol, its oxidation produces acetone, a compound which is classified as a ketone.

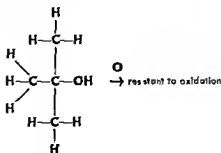


The ketones are not easily oxidized. More powerful oxidizers than those considered here will attack ketones, but in so doing deep seated decomposition sets in with the formation of products having fewer carbon atoms in the molecule. Notice in the secondary alcohols that the carbon atom to which the alcohol group is attached carries but one hydrogen, and this is removed in forming the ketone. The use of general formulas leads to the following equation.



As a summary, the oxidation of a secondary alcohol produces a ketone. Ketones in turn resist oxidation.

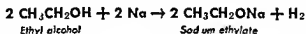
Molecules of tertiary alcohols have no hydrogen attached to the carbon atom which carries the alcohol group. Tertiary alcohols are consequently resistant to oxidation. Powerful oxidizers break them down into molecules which contain a fewer number of carbon atoms than the tertiary alcohols themselves. The simplest of the tertiary alcohols is tertiary butyl alcohol.



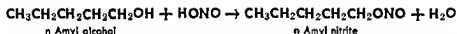


**Other Reactions of Alcohols:**

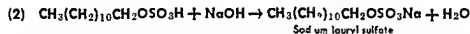
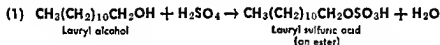
In some alcohols, particularly the primary ones, the hydrogen of the alcohol radical can be replaced by very active metals



Alcohols react with acids, both inorganic and organic, to produce "ethereal salts," more commonly called esters. Nitrous acid reacts with *n*-amyl alcohol to give the ester *n*-amyl nitrite. This compound has use in medicine as a vasodilator in angina pectoris. Since it relaxes bronchial muscles, *n*-amyl nitrite is useful in treating asthma.



The sulfuric acid ester of lauryl alcohol is of interest because its sodium salt is an important detergent. The steps in its manufacture are as follows:



Sodium lauryl sulfate and similar compounds are widely used as soapless detergents.

The behavior of alcohols with organic acids will be considered later after the carboxylic acids have been studied.

Alcohols are starting materials for the preparation of ethers. In a later section of this chapter it will be shown how ethyl ether is manufactured from ethyl alcohol.

In addition to the reactions of the alcohols which have been discussed here there are many others. A number of the alcohols are cheap, readily available compounds, and they are sufficiently reactive to serve as raw materials for synthesizing a variety of more complex organic compounds.

**Two Important Monohydric Alcohols:**

Methyl alcohol and ethyl alcohol are of sufficient importance to warrant individual attention.

The scientific name for methyl alcohol is methanol, and this has come into rather general usage. Methyl alcohol is also known as wood alcohol because at one time an important source was a liquid called pyroligneous acid which is produced in the destructive distillation of wood. Today the important source is synthesis from carbon monoxide and hydrogen. These gases are mixed in proper proportions and heated at 400° C. and 150 atmospheres of pressure in the presence of a catalyst.



Methyl alcohol is a colorless liquid which boils at 65° C. It is miscible with water in all proportions. The vapors of this alcohol burn readily with a hot blue flame. Methanol is highly poisonous. In the body it is oxidized to toxic formic acid which will paralyze the optic nerves and lead to blindness. Death may ensue from larger amounts; two to four ounces are usually fatal.

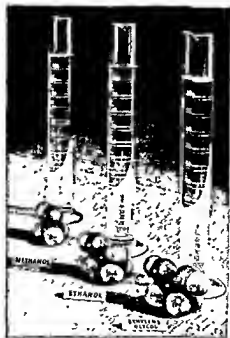
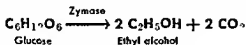


Fig 2—Three Important Alcohols. The models show the molecular structure of these three alcohols. The dihydric alcohol, called ethylene glycol, is an excellent antifreeze solution for automobile radiators. Why is it better for this purpose than the other two alcohols? Courtesy, Carbide and Carbon Chemicals Corp.

Despite its poisonous nature large quantities of methyl alcohol are produced to supply industrial demands. In the field of paints and varnishes it is a solvent for shellacs and resins. Considerable quantities are used as antifreeze.

Ethyl alcohol is produced by fermentation of sugars which in turn frequently come from the hydrolysis of starch. Barley and corn have long been used to supply starch for this purpose. This has resulted in the name *grain alcohol* for ethyl alcohol. Thus, glucose sugar in the presence of yeast which supplies the enzyme called zymase is fermented to give ethyl alcohol and carbon dioxide



Glucose can be obtained by hydrolyzing most varieties of starch. Much of the industrial ethyl alcohol produced in this country comes from fermentation of the sugars present in molasses, the latter a by product from the refining of sugar.

Another important present day source of ethyl alcohol is its synthesis from ethylene  $\text{CH}_2 = \text{CH}_2$ , an unsaturated hydrocarbon which is formed in the cracking of petroleum oil. Notice that the molecular formulas for ethylene and ethyl alcohol differ by  $\text{H}_2\text{O}$ . Ethylene does not add water directly to give ethyl alcohol, yet chemists have learned how to accomplish this indirectly, and very efficiently.

In scientific nomenclature ethyl alcohol is called ethanol. This alcohol is a colorless liquid which boils at  $78^\circ \text{C}$ , and like methyl alcohol it is soluble in water in all proportions.

Ethanol is the alcohol which is present in alcoholic beverages. In these the per cent of alcohol by volume ranges from 3 to 4 per cent in beer to as high as 55 per cent in whisky and brandy. In the body, ethyl alcohol is quickly absorbed without digestion and then oxidized to carbon dioxide and water with the production of seven Calories of heat energy for each gram of alcohol. While controlled amounts of ethyl alcohol are valuable medicinally as a stimulant in conditions of shock and collapse, it is a scientific fact that excessive use of alcoholic beverages has highly undesirable effects. Initially it produces an increase in respiration and a rise in blood pressure, but shortly there follows a drop below normal. Taken internally in large amounts ethyl alcohol causes impairment of mental processes and a loss of muscular coordination. Any indi

vidual in such a state who is driving an automobile becomes a potential killer. It is well known that continued unrestricted use of ethyl alcohol leads to chronic alcoholism.

### ETHYL ALCOHOL IN BEVERAGES

<i>Distilled (40 to 60 per cent Alcohol)</i>	<i>Undistilled (3 to 10 per cent Alcohol)</i>
<i>Brandy from wine</i>	<i>Beer from fermented malt and hops</i>
<i>Whiskey* from fermented malt solution</i>	<i>Ale from fermented malt and hops</i>
<i>Rum from fermented molasses</i>	<i>Wine from fermented fruit juice</i>
<i>Gin from whiskey flavored with juniper</i>	Added alcohol makes fortified wines as port (15-18%) and sherry (18-21%)

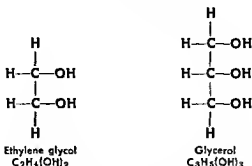
\* Whiskey is a distillate obtained from grains that have been ground into meal, mixed with water and malted grains, cooked to a mash, yeast added, and then fermented for 72 hours.

Ethanol in 50 to 70 per cent concentration is a disinfectant widely used in hospitals for surface application. It destroys organisms by coagulating protoplasm. Preparations known as tinctures and spirits contain this alcohol as the solvent. Denatured alcohol is made by adding to ethanol small quantities of substances which render it unsuitable for drinking. Certain types of denatured alcohol are used externally as rubbing liquids; however, isopropyl alcohol has been supplanting ethyl alcohol for this use.

Second to water, ethanol is the most widely used of all solvents. It is also an important starting material for manufacturing other organic compounds.

### Polyhydric Alcohols

Compounds which have two alcohol groups in their molecules are known as glycols. The simplest and most important of these is ethylene glycol, which is a primary alcohol twice over. It has a relatively high boiling point of 197° C and is soluble in water in all proportions. Ethylene glycol has wide usage as a permanent antifreeze for automobile radiators and is sold for this purpose under such trade names as Prestone and Zerex. Ethylene is the starting material for the preparation of this dihydric alcohol.



Glycerol is a trihydric alcohol as evidenced by its structural formula. Important sources of glycerol are the animal and vegetable fats and oils. In the manufacture of soap these natural fats and oils are saponified, and glycerol appears as a by-product. More recently, methods have been perfected for synthesizing glycerol from propylene,  $\text{CH}_3-\text{CH}=\text{CH}_2$ .

Glycerol is a clear viscous liquid of sweet taste. It is hygroscopic and soluble in water. Since glycerol is nontoxic it may be used as a solvent in the preparation of certain medicines, and its nontoxic character coupled with the fact that it is hygroscopic accounts for its wide usage in lotions and other cosmetics. Nitroglycerine, one of the important explosives, is made by reacting glycerol with nitric acid. Inasmuch as this substance is an ester of glycerol it is more correctly called glyceryl trinitrate. Dynamite contains glyceryl trinitrate.

### SELF-TESTING QUESTIONS

- 1 Name four fundamental types of organic compounds which contain carbon, hydrogen, and oxygen.
- 2 What is an alcohol?
- 3 How are the saturated monohydric alcohols classified?
- 4 What is produced when the primary alcohol is oxidized with an aqueous oxidizer? What is formed from the secondary alcohol?
- 5 In what chemical characteristic does the tertiary alcohol differ from the primary and the secondary?
- 6 Compare and contrast the physical properties of the lower and the higher alcohols.
- 7 What is the physiological effect of small amounts of grain alcohol? of large amounts?
- 8 Why is methyl alcohol more poisonous than ethyl alcohol?
- 9 What are glycols? What is the simplest one?
- 10 Are alcohols bases? How does the alcohol differ from the inorganic base?

- 11 What is the nature of a homologous series of compounds?
- 12 Which is correct *n* Propyl and isopropyl alcohols are isomers or are homologues?
- 13 What is the most important source of industrial methyl alcohol?
- 14 What two methods of preparation provide industrial ethyl alcohol?
- 15 Why is glycerol an important ingredient in many brands of hand lotion?

## II. THE ALDEHYDES

### Nature of Aldehydes:

We have learned that the aldehydes are the first oxidation products of the primary alcohols, and this is an important method for their preparation. The following table gives the first few members in the homologous series of aldehydes.

#### ALDEHYDES

<i>Name</i>	<i>Formula</i>	<i>Number of Structures</i>
Formaldehyde	HCHO	1
Acetaldehyde	CH <sub>3</sub> CHO	1
Propionaldehyde	CH <sub>3</sub> CH <sub>2</sub> CHO	1
Butyraldehydes etc	C <sub>3</sub> H <sub>7</sub> CHO	2

$$\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{O} \end{array}$$

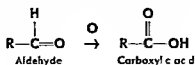
All aldehydes possess the  $-\text{C}=\text{O}$  structure, commonly known as the aldehyde group. The general formula for the aldehydes becomes

$$\begin{array}{c} \text{H} \\ | \\ \text{R}-\text{C}=\text{O} \end{array}$$

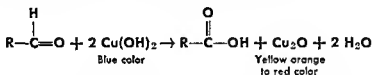
where R is hydrogen in the case of formaldehyde, but a hydrocarbon radical for all others. Notice that two butyraldehydes exist, one is called *n*-butyraldehyde and its isomer is known as isobutyraldehyde. It is suggested that the reader write the structural formulas for these two compounds.

### The Oxidation of Aldehydes:

In discussing the oxidation of primary alcohols it was shown that aldehydes are easily oxidized to give carboxylic acids, hence, aldehydes are reducing agents.



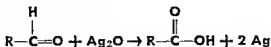
Aldehydes will reduce cupric ion ( $\text{Cu}^{++}$ ) to cuprous ion ( $\text{Cu}^{+}$ ) Fehling's solution and Benedict's solution both provide cupric copper, in the form of cupric hydroxide, for this kind of reaction. Ordinarily cupric hydroxide is insoluble, but the solutions just named contain tartrates and citrates which are effective in preventing the separation of  $\text{Cu}(\text{OH})_2$ . The behavior of either one of these solutions is shown in the following equation:



Both Fehling's and Benedict's solutions have a clear blue color. A positive test is recognized by the formation of insoluble cuprous oxide, red in color. Notice that as the aldehyde is oxidized to the acid the cupric copper in the reagent is reduced in valence from +2 to +1 in  $\text{Cu}_2\text{O}$ . Fehling's reagent is prepared as two separate solutions to be mixed just before use. Benedict's reagent is a single solution, hence more convenient to use, and this fact together with its somewhat greater sensitivity makes it the preferred reagent.

The sugar glucose (blood sugar) contains an aldehyde group and therefore gives a positive response with Fehling's and Benedict's solutions. This provides a simple rapid clinical test for blood sugar in the urine.

Similarly, aldehydes will reduce silver ions to metallic silver. Tollen's reagent contains a compound of silver which provides silver ions for this type of test. The following equation expresses the essentials of this reaction:



By proper techniques the silver metal can be deposited on the sides of the container as a silver mirror.

The above reactions may be used to differentiate aldehydes from

ketones The ketones are sufficiently resistant to oxidation to be unaffected by these reagents

### Polymers from Aldehydes

In addition to being excellent organic reducing agents the aldehydes form polymers When a water solution of formaldehyde is treated with a trace of sulfuric acid and then evaporated to dryness a solid residue appears The solid is a polymer of the aldehyde which contains from ten to as many as one hundred molecules linked together into one large molecule It is known as paraformaldehyde, and since it releases formaldehyde vapors when heated it is used in the form of candles and in lamps for disinfecting purposes There are also other polymers of formaldehyde

Acetaldehyde under the catalytic influence of sulfuric acid polymerizes to a liquid called paraldehyde This substance is constructed from three molecules of the aldehyde and is designated by the formula  $(\text{CH}_3\text{CHO})_3$  Paraldehyde has medicinal value as a soporific

Polymerization is not confined to the two aldehydes just considered, but rather it is a general behavior of this class of compounds

### Two Important Aldehydes

Formaldehyde and acetaldehyde the first two members in the series of saturated aliphatic aldehydes are sufficiently important to be discussed further

Formaldehyde can be prepared by the controlled oxidation of methyl alcohol At room conditions this aldehyde is a gas which possesses a sharp penetrating odor The water solution which contains 37 to 40 per cent of formaldehyde is known as formalin This solution hardens tissue by coagulating the protein and for this reason it is used as a preservative for biological specimens

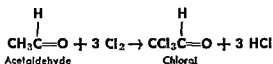
The reaction of formaldehyde with ammonia gives a solid compound called urotropine,  $(\text{CH}_2)_6\text{N}_4$  Urotropine is stable in the presence of alkalis, but it decomposes in acid media to produce formaldehyde For many years it has been an important urinary antiseptic, but recently sulfa drugs have to some extent replaced it

Acetaldehyde is the first oxidation product from ethyl alcohol Another source is synthesis from acetylene Acetaldehyde is a liquid of sharp odor which boils at  $21^\circ\text{C}$ , just slightly below usual room temperature

Chlorine reacts with acetaldehyde in a substitution type of re



action to give chloral, an oily liquid. With water, chloral forms a white solid, chloral hydrate. This substance is a powerful hypnotic, added to alcoholic beverages it constitutes the so called knockout drops.



### SELF-TESTING QUESTIONS

- 16 What are the steps in the oxidation of the primary alcohol?
- 17 What characteristic group is found in all aldehydes?
- 18 Why is the Benedict test of clinical importance?
- 19 How is it possible to distinguish between aldehydes and ketones?
- 20 What are the properties and uses of formaldehyde?
- 21 What are the properties and uses of acetaldehyde?
- 22 What is produced when an aldehyde is oxidized?
- 23 What is an important substitution product of acetaldehyde? For what is it used?
- 24 In what way is formaldehyde related to paraformaldehyde?
- 25 Embalming fluids contain formaldehyde. Why is this?

## III. THE KETONES

### The Structure and Nature of Ketones:

The ketones are oxidation products of the secondary alcohols and conform to the type formula  $\text{R}-\text{C}-\text{R}'$ . Several of the first



members in the series are given in the table. Notice that the ketones are commonly named by designating the two hydrocarbon radicals

which are attached to the  $\text{>C=O}$  group, known as the carbonyl

### KETONES

Name	Condensed Structural Formula
Dimethyl ketone	$\text{CH}_3\text{COCH}_3$
Methyl ethyl ketone	$\text{CH}_3\text{COC}_2\text{H}_5$
Diethyl ketone	$\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$
Methyl n propyl ketone	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$
Methyl isopropyl ketone	$\text{CH}_3\text{COCH}(\text{CH}_3)_2$
etc	

} isomers

group This same group is found also in the aldehydes, where at least one of the attached factors must be a hydrogen atom (In formaldehyde both attachments to the carbonyl are hydrogen atoms) In the ketones the carbonyl always carries two hydrocarbon radicals which may be the same (simple ketones) or different (mixed ketones)

The ketones are far less reactive than the aldehydes They are sufficiently resistant to oxidation to be unaffected by Fehling's and Benedict's reagents This difference in reactivity of aldehydes and ketones is due primarily to the fact that in the ketones there is no hydrogen attached to the carbonyl group When ketones are oxidized by powerful oxidizers the carbon chain is broken and carboxylic acids with fewer carbon atoms are formed \*

### An Important Ketone

The most important ketone is the simplest one, dimethyl ketone, better known as acetone The oxidation of isopropyl alcohol produces this compound Acetone is a volatile liquid with a boiling point of  $56^{\circ}\text{C}$  It is readily soluble in water Industrially this ketone is one of the important solvents, particularly suitable for dissolving fats oils resins, and gums Adhesive tape can be removed with acetone

It is interesting to note that acetone is normally present in the blood in very small amounts Larger quantities of acetone in the blood and urine are indicative of a faulty fat metabolism This may be evidenced as diabetes mellitus (sugar diabetes) In severe cases of this affliction the amount of acetone produced is sufficient for its detection in the breath and the urine by reason of its characteristic sweetish odor

### SELF-TESTING QUESTIONS

- 26 How does the ketone differ from the aldehyde in structure?
- 27 What is the carbonyl group? Do both aldehydes and ketones contain this group?
- 28 How is the ketone related to the secondary alcohol?
- 29 How do aldehydes and ketones compare in ease of oxidation?
- 30 What is the structural formula for acetone? Why is it the simplest possible ketone?



## IV. THE ETHERS

## Nature of Ethers:

Because of the presence of the hydroxyl group in the alcohol it becomes possible to link together two alcohol molecules by dehydration (loss of water) and form new structures called ethers. There are many ethers, yet all of them are based on the type formula  $R-O-R'$ . They may therefore be looked upon as oxides of an organic character. In theory an ether may be viewed as the result of replacing the hydrogen of the  $-OH$  group of the alcohol by an  $R$  group, or as the result of replacing both hydrogens of the water molecule with  $R$  groups.

The accompanying table gives names and formulas for a number of the lower molecular weight ethers.

ETHERS

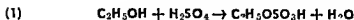
Name	Condensed Structure
Dimethyl ether	$CH_3-O-CH_3$
Methyl ethyl ether	$CH_3-O-CH_2CH_3$
Diethyl ether	$CH_3CH_2-O-CH_2CH_3$
Methyl n propyl ether	$CH_3-O-CH_2CH_2CH_3$
Methyl isopropyl ether	$CH_3-O-CH(CH_3)_2$
etc	

The last three ethers listed in the table are isomers, all have the same molecular formula,  $C_4H_{10}O$ . Those ethers which have the same radical for  $R$  and  $R'$  are classified as simple ethers. When different radicals are attached to the oxygen the substance is a mixed ether. Notice that two simple and three mixed ethers appear in the table. The characteristic linkage in the ether molecule is  $C-O-C$ .

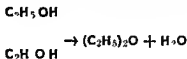
Ethers are but slightly soluble in water, and the solubility decreases rapidly with increasing molecular weight. Ethyl ether (diethyl ether) is soluble in water to the extent of only about 7 per cent, it is a highly volatile liquid which boils at  $35^\circ C$ , a temperature not far above room temperature, and actually below that of the body.

## Preparation and Properties of Ethyl Ether

Diethyl ether, ordinarily called ethyl ether or simply ether, is the most important. It can be prepared quite efficiently from ethyl alcohol by reaction with sulfuric acid.



The equations describe the two steps in the process. An inspection of these equations shows that the net result is the elimination of a molecule of water from two molecules of ethyl alcohol



The function of the sulfuric acid is to accomplish this type of dehydration

Chemically the ethers are quite inert. For example, they fail to react with sodium metal, aqueous oxidizers, strong alkalies, and cold mineral acids. However, ethers are combustible, the lower molecular weight ones are highly flammable, and their vapors form explosive mixtures with air. This inherent danger must be kept in mind when using ethyl ether for solvent purposes, or as an anesthetic.

Although ethyl ether is known to most people simply as ether, the student of chemistry finds that it is but one of many compounds classified as ethers. Ethyl ether and isopropyl ether in particular are widely used as solvents or extractives for fats, oils, resins, etc. However, their volatility, flammability, and explosive nature when mixed with air make these ethers, and the other lower members of the series, exceedingly hazardous to work with.

Of all the anesthetics, ether requires less skill in its administration and its margin of safety is greater. It is slower in its action, but more lasting in its effects, and causes a greater relaxation of the muscles than does nitrous oxide, chloroform, or ethylene. Moreover, during ether anesthesia the pulse, respiration, and blood pressure of the patient remain normal or slightly above. The occasional nausea of the patient and the irritating action on the kidneys and respiratory system are the main objections to its use. To a considerable extent ether has been replaced by more pleasant anesthetics such as nitrous oxide, oxygen, and ethylene oxygen, and others. Ether for anesthesia is marketed in special containers.



Fig. 3—The Comforting Oblivion of Anesthesia. A surgical operation prior to the latter half of the 19th century was a horrible ordeal. What anesthetic could be given by the above method? Courtesy, Perke, Davis & Co., N. Y. C.

### Anesthetics:

Thus far a number of relatively simple compounds have been studied which have value as anesthetics. Choice is governed by a number of factors; nature of the surgery and the physical condition and tolerances of the patient are of course of primary consideration. On occasions it is desirable to start anesthesia with one substance, or combination of substances, and then later to change over to others. Thus vinyl ether, called Vinethene, is at times used as an induction agent in general anesthesia prior to ethyl ether.

The anesthetics listed in the table on page 304 are with one exception organic compounds.

### SELF-TESTING QUESTIONS

31. How does the structure of an ether compare with that of an alcohol of water?
32. How does a simple ether differ from a mixed ether?
33. What is the method of preparation for ethyl ether?
34. What are the important uses of ethyl ether?
35. Why are the lower ethers dangerous to work with?
36. What are the advantages and the disadvantages of ethyl ether as an anesthetic?

- 37 Which compound given in the table of anesthetics is not organic?  
 38 Why can ethers be called hydrocarbon oxides?  
 39 Are diethyl ether and methyl n propyl ether homologues? are they isomers?  
 40 How does ethyl ether compare with ethyl alcohol in water solubility?

### SOME ANESTHETICS

<i>Name</i>	<i>Formula</i>	<i>Remarks</i>
Chloroform	$\text{CHCl}_3$	Nonflammable and nonirritating Has gradually been replaced by others
Cyclopropane	$\text{C}_3\text{H}_6$	General inhalation anesthetic Quick acting nonirritating no ill after effects
Ethyl chloride	$\text{CH}_3\text{CH}_2\text{Cl}$	Local anesthetic rapid evaporation freezes tissue Not often used as an inhalation anesthetic
Ethylene	$\text{CH}_2 = \text{CH}_2$	Excellent muscular relaxation rapid recovery
Ethyl ether	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	See discussion elsewhere in this section
Nitrous oxide	$\text{N}_2\text{O}$	Used in dentistry and minor surgery
Vinyl ether	$\text{CH}_2 = \text{CHOCH} = \text{CH}_2$	Convenient for short anesthesia May be used with $\text{N}_2\text{O}$ and with ethylene for better relaxation.

### SUGGESTED ACTIVITIES

#### I THOUGHT PROVOKING QUESTIONS

- 1 Why is formaldehyde a more powerful reducing agent than acetone?
- 2 Why do some sugars act in the capacity of reducing agents?
- 3 Why is grain alcohol used extensively by the pharmacist?
- 4 What significance is attached to excessive acetone in the urine?
- 5 Why is formic acid easily oxidized whereas acetic acid is not?
- 6 Do all types of alcohols give carboxylic acids when treated with aqueous oxidizing agents? Discuss
- 7 How do ethers compare in chemical activity with (1) aldehydes (2) ketones (3) saturated hydrocarbons?
- 8 How do you account for the fact that continued use of acetone to remove liquid nail polish causes the nails to become brittle?
- 9 Under what conditions is ethanol considered to be a poison?
- 10 When aldehydes are made by oxidizing primary alcohols why must they quickly be removed from the presence of the oxidizer?

## II VOCABULARY TESTING OF NEW TERMS

alcohol	ketone	polyhydric alcohol
primary alcohol	carboxylic acid	ethereal salts
secondary alcohol	polymerization	zymase
tertiary alcohol	carbonyl	formalin
carbonyl	mixed ether	aldehyde
ether	simple ether	induction anesthetic

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 The Physiological Effects of Ethyl Alcohol
- 2 General Anesthesia
- 3 Industrial Uses of Alcohols
- 4 Clinical Testing for Blood Sugar

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on page 714

# THE CARBOXYLIC ACIDS AND THEIR SALTS AND ESTERS. SOME CYCLIC COMPOUNDS

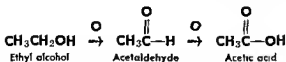
## CHAPTER OUTLINE

- |   |                                     |
|---|-------------------------------------|
| I CARBOXYLIC ACIDS                              | (b) Chemical reactions              |
| (a) General characteristics of carboxylic acids | III AROMATIC COMPOUNDS              |
| (b) Chemical properties of carboxylic acids     | (a) The aromatic ring               |
| (c) Formic and acetic acids                     | (b) Some typical aromatic compounds |
| (d) Polybasic carboxylic acids Hydroxy acids    | IV HETEROCYCLIC COMPOUNDS           |
| II ESTERS                                       | (a) The heterocyclic ring           |
| (a) The nature of esters                        | (b) Some heterocyclic compounds     |

## I. CARBOXYLIC ACIDS

### General Characteristics of Carboxylic Acids:

In the preceding chapter it was shown that the oxidation of a primary alcohol produces first an aldehyde, and that the aldehyde in turn is readily oxidized to a carboxylic acid. Using O to indicate oxygen from an aqueous oxidizing agent, for example, potassium dichromate solution acidified with sulfuric acid, the following formulas picture the steps in the formation of acetic acid from ethyl alcohol:



From this it should be apparent that carboxylic acids can be made by the oxidation of primary alcohols or aldehydes as the starting materials. Usually the alcohol is the more available.

The general formula for monobasic carboxylic acids, known also

as fatty acids, is  $\text{R—}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{—OH}$ . The  $\text{—}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{—OH}$  group, which is the characteristic structural features of all carboxylic acids, is called the *carboxyl group*. As will become apparent, the properties of the carboxylic acids stem largely from this group.

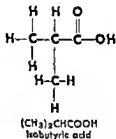
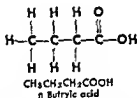


The table gives the names for the first several members in the series of saturated aliphatic acids which have one carboxyl group per molecule

### ALIPHATIC MONOBASIC CARBOXYLIC ACIDS

Name	Formula	Possible Structures
Formic acid	HCOOH	1
Acetic acid	CH <sub>3</sub> COOH	1
Propionic acid	CH <sub>3</sub> CH <sub>2</sub> COOH	1
Butyric acids	C <sub>3</sub> H <sub>7</sub> COOH	2
Valeric acids	C <sub>4</sub> H <sub>9</sub> COOH	4
etc		

Note from the table that, beginning with the butyric acids, isomerism becomes a characteristic of this homologous series. The two butyric acids are identified by the following structural formulas and names

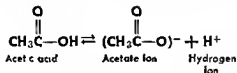


In this series of acids the first members are clear liquids, those above nine carbon atoms of normal chain structure are solids. Two higher members of this series, not given in the table, are palmitic and stearic acids, formulas C<sub>15</sub>H<sub>31</sub>COOH and C<sub>17</sub>H<sub>35</sub>COOH, respectively. These two solid acids are found in the structures of many animal and vegetable fats and oils in the form of glyceryl esters.

The lower fatty acids are completely soluble in water, but starting with the valeric acids solubility in water decreases rapidly with increasing molecular weight. Formic, acetic, and propionic acids have sharp odors. Beginning with the butyric acids those which are sufficiently volatile have extremely disagreeable odors. The odor of rancid butter is due to free butyric acid.

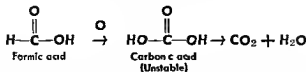
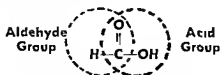
### Chemical Properties of Carboxylic Acids:

The carboxylic acids vary somewhat in strength, but in general they are classified as weak acids. This means that the water soluble ones dissociate only to a small degree to give hydrogen ions. (Recall that the strength of an acid is measured in terms of its dissociation to provide free hydrogen ions.) Acetic acid, for example, in a 5 per cent aqueous concentration, is ionized to the extent of about 1.5 per cent. Notice that in the ionic dissociation

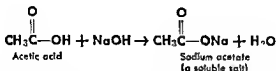


the hydrogen ion comes from the carboxyl group of the acid, other hydrogens present in the molecule are not the source of hydrogen ions. While the carboxylic acids are relatively weak, they are nevertheless stronger than carbonic acid. Solutions of the soluble carboxylic acids have the characteristic sour taste and redden blue litmus paper.

Carboxylic acids, excepting formic, are quite resistant to oxidation by aqueous oxidizers. Formic acid is very easily oxidized. An examination of its structure shows that unlike its homologues this acid has a hydrogen atom attached directly to the carboxyl radical, hence, formic acid possesses the character of an aldehyde as well as that of the carboxylic acid.

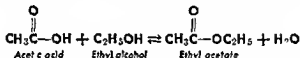


A typical reaction of carboxylic acids is salt formation. This can be accomplished by treating the acid with a base in a neutralization type of reaction. In this manner, sodium acetate can be made from acetic acid.

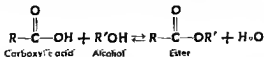


Many of the salts of carboxylic acids are water soluble and highly ionized, hence strong electrolytes. Some have value in medicine. The table on page 312 gives names, formulas, and uses for a number of typical salts derived from organic acids.

Carboxylic acids react with alcohols to give a class of compounds known as organic *esters*. A well known liquid ester is ethyl acetate, prepared from ethyl alcohol and acetic acid. This type of reaction shows some similarity to inorganic reactions of neutralization, and accounts for the older name, *etheral salt*, for the ester.



The preparation of an ester in this manner illustrates a type of organic reaction which does not go to completion, but instead reaches a point of chemical equilibrium. When ethyl alcohol and acetic acid are brought together in equal molar quantities the equilibrium is established after about two thirds of each has reacted. In order to get the reaction to progress further in the direction of completion, i.e., ester formation, something must be done to "upset" the ester equilibrium. For example, the continuous removal of the water or the ester from the reaction mixture. Reactions which attain equilibrium, and therefore do not go to completion, are frequently encountered in organic chemistry. More will be mentioned about esters in a later section, notice, however, that this type of reaction can be written in terms of general formulas

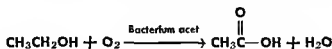


### Formic and Acetic Acids

Formic acid is somewhat stronger than its homologues. It is a clear liquid which boils at 101° C. Contact of this acid with the skin causes blisters, the stinging sensation and blistering which result from the bites of insects such as bees, mosquitos, and ants is due to the injection of formic acid through the skin. The irritation

can be relieved by washing the affected area with soap or dilute ammonia water to neutralize the acid. In industry, formic acid is employed in processes for dyeing textiles, and for removing hair from hides.

Acetic acid is the acid of vinegar. Cider vinegar is produced by the oxidation of the ethyl alcohol which is present in "hard" cider.



Vinegar contains from 4 to 5 per cent of acetic acid.

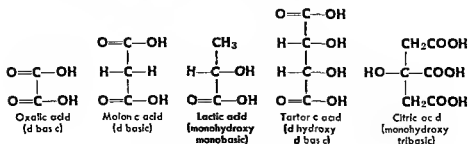
Glacial acetic acid is practically free from water and approximately 99.5 per cent pure  $\text{CH}_3\text{COOH}$ . It is so called because it freezes to an ice-like solid at  $16.7^\circ\text{C}$ . This acid is undoubtedly the best known and most widely used of the carboxylic acids. In industry it has value as a solvent and as a starting material for synthesizing numerous other organic compounds.

### Polybasic Carboxylic Acids. Hydroxy Acids.

The organic acids dealt with thus far have contained one carboxyl group and hence one ionizable hydrogen in the molecule. There are some acids which have two carboxyl groups in the molecule, some with three, etc. Oxalic acid, with two carboxyl groups, is a dibasic acid, and citric acid, with three carboxyl groups, is tribasic.

The hydroxy acids include monobasic and polybasic carboxylic acids which also contain one or more hydroxyl groups in the molecule. A number of the fruit acids are hydroxy acids. For the most part the hydroxy acids exhibit a chemical behavior which is characteristic of the carboxyl group and of the type of alcohol structure which is present.

Following are the names and structures for a few polybasic and hydroxy acids. While the student may not be expected to write some of these more complex structures, it should be realized that those which appear here are important ones.



Oxalic acid is a white crystalline, water soluble solid, actual composition  $(\text{COOH})_2 \cdot 2 \text{H}_2\text{O}$ , hence a dihydrate. It is the strongest of the carboxylic acids, and this property must be observed in using it. Oxalic acid occurs in nature in the form of salts in certain plants, for example, rhubarb and sorrel. Like other dibasic acids it forms two series of salts, i.e., acid salts and normal salts.

Lactic acid is produced when milk sours, it is found also in sauerkraut. We shall learn later that lactic acid plays a role in metabolism, and that it is a normal constituent of muscle tissue.

Citric and tartaric acids are important fruit acids, and the former, as its name implies, is found in citrus fruits. Tartaric acid, free and also in the form of salts, occurs in grapes, and in the deposits which form in wine casks.

The accompanying table presents some of the typical salts of a number of organic acids.

#### SALTS OF CARBOXYLIC ACIDS

<i>Name</i>	<i>Formula</i>	<i>Uses</i>
Calcium lactate	$(\text{CH}_3\text{CHOHCOO})_2\text{Ca}$	Medicinally for calcium deficiency
Calcium propionate	$(\text{CH}_3\text{CH}_2\text{COO})_2\text{Ca}$	Prevention of molding of bread
Lead acetate	$(\text{CH}_3\text{COO})_2\text{Pb}$	Treating poison ivy, skin rashes
Magnesium citrate	$\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2$	Saline purgative
Potassium acid tartrate (cream of tartar)	$\text{KH C}_4\text{H}_4\text{O}_6$	Tartrate baking powders
Sodium citrate	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	Prevention of blood clotting in transfusions
Zinc stearate	$(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Zn}$	Dusting powders ointments

The amino acids are substituted carboxylic acids. Because of their close association with proteins the amino acids are more profitably discussed in a later chapter.

#### SELF-TESTING QUESTIONS

1. What is the name and the structure of the characteristic group of a carboxylic acid?
2. How do organic acids compare with inorganic acids in respect to ionization and acid properties?

- 3 What are three important chemical properties of carboxylic acids?
- 4 Which carboxylic acids are of outstanding importance? Why?
- 5 What are three important hydroxy acids? How many carboxyl groups does each contain?
- 6 How does oxalic acid compare in strength with other carboxylic acids? What must be true about its ionization?
- 7 Which salts of organic acids have use in medicine? In what way?
- 8 How would you proceed to make calcium lactate by a neutralization method?

## II. ESTERS

### The Nature of Esters:

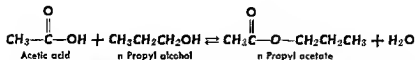
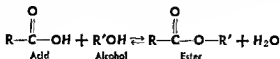
In discussing the carboxylic acids it was pointed out that the esters have the general formula  $\text{RCOOR}'$ . For those esters which are derived from formic acid the first R in the generalized formula is a hydrogen atom. For all other esters both R and R' are hydrocarbon radicals.

### SOME ESTERS

Name	Formula
Methyl formate	$\text{H}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{CH}_3$
Methyl acetate	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{CH}_3$
Ethyl acetate	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{CH}_2\text{CH}_3$
Methyl propionate	$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{CH}_3$
n Propyl acetate etc	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$

The most used method for the preparation of the ester is by direct reaction between the carboxylic acid and the alcohol. This approach is termed *esterification*. A trace of sulfuric acid is often used to catalyze the process, larger amounts of sulfuric acid absorb the water produced, and shift the equilibrium in the direction of ester formation. In the equations which follow for esterification

the first one is in general terms. Observe how this then applies specifically to the synthesis of *n* propyl acetate



Numerous esters are found in nature and they account for the fragrant odors of many flowers and fruits. Their pleasant odors make them valuable for use in perfumery and in the preparation of synthetic flavorings. Some esters, for example, ethyl acetate and butyl acetate, are important solvents in lacquers. Finger nail polish illustrates such a use.

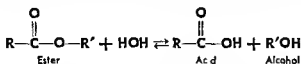
### ODORS OF ESTERS

Name	Formula	Odor
Amyl acetate	$\text{CH}_3\overset{\text{O}}{\parallel}\text{C}-\text{O}-(\text{CH}_2)_4\text{CH}_3$	Apricot
Amyl butyrate	$\text{CH}_3(\text{CH}_2)_2\overset{\text{O}}{\parallel}\text{C}-\text{O}-(\text{CH}_2)_4\text{CH}_3$	Pear
Ethyl butyrate	$\text{CH}_3(\text{CH}_2)_2\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{CH}_2\text{CH}_3$	Pineapple
Ethyl formate	$\text{HC}\overset{\text{O}}{\parallel}-\text{O}-\text{CH}_2\text{CH}_3$	Rum
Isoamyl acetate	$\text{CH}_3\overset{\text{O}}{\parallel}\text{C}-\text{O}-(\text{CH}_2)_3\text{CH}(\text{CH}_3)_2$	Banana
Octyl acetate	$\text{CH}_3\overset{\text{O}}{\parallel}\text{C}-\text{O}-(\text{CH}_2)_7\text{CH}_3$	Orange

### Chemical Reactions

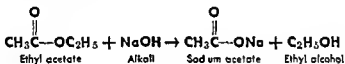
Esters are essentially neutral compounds and they are not as reactive as the acids and alcohols from which they are prepared.

Two rather closely related reactions of esters will be considered, these are *hydrolysis* and *saponification*. In hydrolysis the ester reacts with water to give a *carboxylic acid* and an *alcohol*. Hydrolysis reactions are usually promoted by use of acids, bases, enzymes, etc., as catalysts. Notice that the hydrolysis of the ester is just



the opposite of its preparation via esterification, and results in an equilibrium.

The saponification of an ester is carried out by the use of strong aqueous alkali, for example, sodium hydroxide solution. Reactions of saponification go to completion. The equation for the saponification of ethyl acetate follows.



The discussion of animal and vegetable fats and oils, which are esters of glycerol and higher fatty acids, is presented in a later chapter. The waxes which are secretions from many plants and animals are also esters. Beeswax from bees, spermaceti from the sperm whale, and lanolin from wool are three important waxes.

### SELF-TESTING QUESTIONS

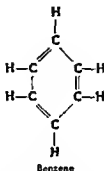
- 9 What are the reactants in the preparation of an ester by the process called esterification?
- 10 Does the reaction for ester preparation via esterification go to completion?
- 11 What is the nature of a reversible reaction? What is true when such a reaction is at a state of equilibrium?
- 12 In the preparation of an ester from an alcohol and a carboxylic acid why does the removal of water upset the equilibrium?
- 13 What is noteworthy about the odors of esters? What value do esters have?
- 14 How does saponification differ from hydrolysis?
- 15 Write the structure for the ester, ethyl formate. What other ester is isomeric with ethyl formate?



### III. AROMATIC COMPOUNDS

#### The Aromatic Ring

We have learned that the aromatic hydrocarbons have a ring or cyclic type of structure, and that the simplest of these hydrocarbons is benzene,  $C_6H_6$ . The structural formula for benzene is as follows



This arrangement of six carbons in a ring, with the alternate single and double bonds, constitutes the so called aromatic or benzene ring structure. In its chemistry benzene does not behave like a highly unsaturated compound. Newer theories suggest that the extra pairs of electrons which are pictured as giving the double bonds are actually uniformly dispersed around the ring so that all six ring bonds, and all six carbon atoms, are equivalent. The most characteristic reaction of the benzene ring is substitution wherein one or more hydrogen atoms are replaced by other atoms or groups of atoms.

For simplicity it is a common practice to indicate the structure of the benzene ring by the use of a hexagon with the alternate single and double bonds. When this notation is used it is understood that at each corner of the hexagon there is a carbon atom,



Benzene  
 $C_6H_6$

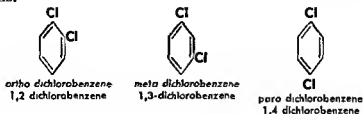


Monochlorobenzene  
 $C_6H_5Cl$

and that each carbon atom has a hydrogen atom attached unless some other atom or group has replaced the hydrogen.

Inasmuch as all six hydrogens of benzene are equivalent it makes

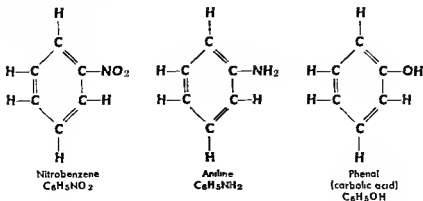
no difference which one is replaced in monosubstitution; only one compound can result. This is illustrated by inspection of the structural formula for monochlorobenzene. However, when two substituents appear, three isomers are possible. The following structural formulas for the three isomeric dichlorobenzenes illustrate this:

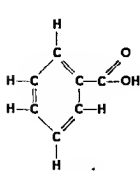


Notice from the structures that there are three possible ways of placing the two substituents, in this case chlorine atoms. When the two substituents are attached to adjacent carbon atoms the structure is identified as *ortho*, abbreviated *o*-. In the *meta* structure, abbreviated *m*-, the substituents are on carbons which are separated by one carbon. For the *para*, abbreviated *p*-, the substituents are attached to carbons which are separated by two carbons. Also, instead of the use of the prefixes *o*-, *m*-, and *p*-, numbers may be used to indicate the positions occupied by substituents. In numbering it is conventional to start with a carbon which carries a substituent and proceed in a clockwise direction around the ring.

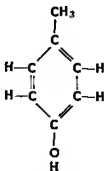
### Some Typical Aromatic Compounds:

A study of aromatic compounds in any detail is beyond the scope and intent of this textbook. However, structures are given in this section for a number of typical aromatic compounds. Some of these have medicinal value.

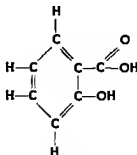




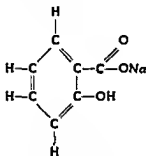
Benzoic acid  
 $C_6H_5COOH$



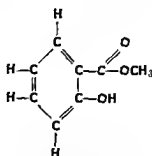
p-Cresol  
 $C_6H_4(CH_3)OH$



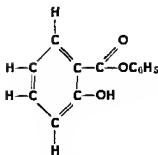
Salicylic acid  
 $C_6H_4(OH)COOH$



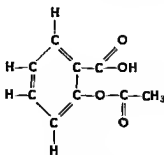
Sodium salicylate  
 $C_6H_4(OH)COONa$



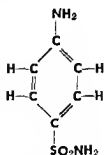
Methyl salicylate  
(oil of wintergreen)  
 $C_6H_4(OH)COOCH_3$



Phenyl salicylate  
(salol)  
 $C_6H_5(OH)COOC_6H_5$



Acetyl ester of salicylic acid  
(aspirin)  
 $C_6H_4(OCOCH_3)COOH$



Sulfanilamide  
(sulf drugs are derived from this compound)

Phenol, commonly called *carbolic acid*, is a highly corrosive and toxic compound. Children have been fatally poisoned by accidentally swallowing phenol; it should never be left in unlocked

medicine cabinets within reach of the very young and unwary. When properly diluted phenol is an excellent disinfectant and antiseptic. The name carbolic acid for phenol must never be confused with a similar name, carbonic acid, which is a harmless solution of carbon dioxide in water.

Sodium salicylate, unlike salicylic acid, is soluble in water. This salt has limited use as a food preservative, for example, in catsups. Medicinally, sodium salicylate is used to relieve rheumatic pain and to reduce fever.

The acetyl ester of salicylic acid is commonly known as aspirin. Several thousand tons are manufactured annually in the United States. Aspirin enjoys wide usage for relieving pain (analgesic) and for reducing fever (antipyretic). Likely its activity is due to the fact that in the body it hydrolyzes to give salicylic acid.

Phenyl salicylate, or salol, is used as an intestinal antiseptic, and also as an antipyretic and antirheumatic. Methyl salicylate, also derived from salicylic acid, is commonly called oil of wintergreen. It finds wide usage as an ingredient in liniments.

### SELF-TESTING QUESTIONS

- 16 What are the structural characteristics of the aromatic ring?
- 17 How many monosubstitution products of benzene are possible? Why?
- 18 Which is the more characteristic reaction of benzene: addition or substitution?
- 19 What is the significance of the prefixes ortho, meta, and para?
- 20 The structure for p-cresol has been given. How many cresols are possible? What are the others?
- 21 How many of the structures given in this section are esters?
- 22 Lysol contains cresols. For what purpose is Lysol used?

## IV. HETEROCYCLIC COMPOUNDS

### The Heterocyclic Ring

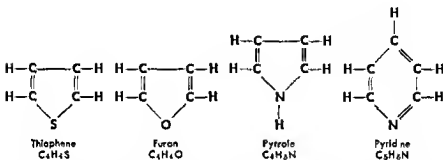
Thus far the cyclic structures dealt with have been confined to rings of carbon atoms. These are termed carbocyclics. In the heterocyclic compounds the ring contains in addition to carbon atoms one or more atoms of other elements. The most important of these are nitrogen, oxygen, and sulfur. Unlike the aromatic ring, the number of atoms constituting the ring of a heterocyclic need not be six.

Heterocyclic compounds have a wide distribution in both plants and animals. Heterocyclic rings appear in some of the more com-

plex molecules, for example, many vitamins, plant pigments, enzymes, alkaloids, and drugs

### Some Heterocyclic Compounds

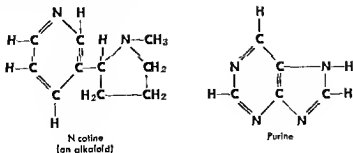
The structures for a number of the illustrative heterocyclic compounds follow

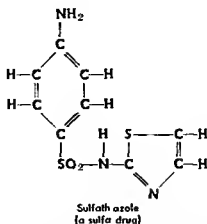


Each of these compounds may be viewed as a parent structure from which numerous derivatives are possible. Thus the pyrrole ring appears in the heme of hemoglobin, and also in chlorophyll. This same ring, in reduced form, constitutes a portion of the structure of the amino acids proline and hydroxyproline. Obviously pyrrole is a hetero ring of considerable biological significance.

The pyridine nucleus is found in several of the alkaloids. One of the B complex of vitamins, nicotinamide, is a derivative of pyridine. Pyridine itself is produced in the destructive distillation of bones.

Some of the heterocyclics, both natural and synthetic, contain two rings in the molecule.





Nicotine consists of a molecule of pyridine joined to a molecule of a reduced pyrrole (pyrrolidine). It is one of the simpler of the alkaloids, and occurs in the tobacco plant.

Purine itself is of little importance, but it has numerous important derivatives. Caffeine and uric acid are two of the better known derivatives of purine. Uric acid is a product of the hydrolysis of nucleic acids which occur in plants and animals as nucleoproteins. Small amounts of uric acid occur in the blood as a metabolic product.

In the structure for sulfathiazole both the aromatic ring and a heterocyclic ring appear. Other sulfa drugs have other groups of atoms in some instances heterocyclic rings in place of the thiazole ring.

### SELF-TESTING QUESTIONS

- 23 How does the carbocyclic differ from the heterocyclic?
- 24 In what classification would you place the aromatic compounds? The cycloparaffins?
- 25 What elements are most usual in the heterocyclic rings?
- 26 What are some of the substances of physiological importance which contain heterocyclic rings?

### SUGGESTED ACTIVITIES

#### I. THOUGHT PROVOKING QUESTIONS

- 1 From an inspection of the structural formulas of formic acid and acetic acid, how may one account for the fact that only formic acid is a reducing agent?
- 2 In what manner is the formation of the ester similar to the inorganic reaction of neutralization? Are ethereal salts similar in properties to inorganic salts?

- 3 How do you explain the fact that metabolism of the fruit acids such as citric acid produces an alkaline effect in the body?
- 4 How does propionic acid ionize in water? What is the equation for its neutralization?
- 5 What products result from the hydrolysis of ethyl n butyrate? What is formed when this ester is saponified?
- 6 Acetic acid and other organic acids of its series will react with sodium carbonate to evolve carbon dioxide. What does this prove about the relative strengths of carboxylic acids and carbonic acid?
- 7 How are the various sulfa drugs related to sulfanilamide?
- 8 What is the food source of the uric acid which is present in small amount in the blood and also in the urine?
- 9 In what respect do hemoglobin and chlorophyll have a similarity of structure?
- 10 Look up the structure of the vitamin known as niacin. How is it related to pyridine?

## II VOCABULARY TESTING OF NEW TERMS

carboxyl group	ortho	carbocyclic
ester	meta	heterocyclic
esterification	para	sulfa drug
hydroxy acid	antipyretic	saponification
aromatic ring	derivative	analgesic

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Esters for Medicinal and Industrial Use
- 2 The Sulfa Drugs
- 3 Medicinal Uses for Salts of Organic Acids
- 4 Some Important Antiseptics and Disinfectants of Aromatic Structure

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on page 714

# CARBOHYDRATES

## CHAPTER OUTLINE

- |   |  |
|---|--|
| <b>I. OCCURRENCE, CLASSIFICATION, AND STRUCTURE OF CARBOHYDRATES:</b> <ul style="list-style-type: none"><li>(a) Occurrence and importance</li><li>(b) Composition and classification</li><li>(c) Structure</li></ul>  | <b>III. PRINCIPAL CARBOHYDRATES</b> <ul style="list-style-type: none"><li>(a) The monosaccharides</li><li>(b) The disaccharides</li><li>(c) The polysaccharides</li></ul>  |
| <b>II. CHEMICAL PROPERTIES OF CARBOHYDRATES:</b> <ul style="list-style-type: none"><li>(a) Reducing properties of carbohydrates</li><li>(b) Hydrolysis of carbohydrates</li><li>(c) Fermentation of carbohydrates</li><li>(d) Oxidation of carbohydrates</li><li>(e) Reaction as alcohols—esterification</li><li>(f) Reduction of carbohydrates</li><li>(g) Form osazones</li></ul> | <b>IV. CELLULOSE:</b> <ul style="list-style-type: none"><li>(a) Physiological uses of cellulose</li><li>(b) Commercial uses of cellulose products<ul style="list-style-type: none"><li>1. Cellulose nitrate</li><li>2. Cellulose acetate</li><li>3. Mercerized cotton</li><li>4. Artificial silk</li><li>5. Cellophane</li><li>6. Paper</li><li>7. Ethyl cellulose, carboxymethylcellulose</li></ul></li></ul> |

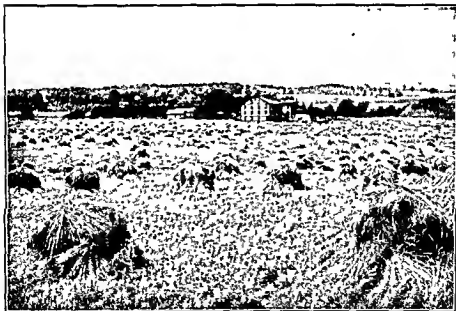


Fig. 1—An Important Source of Carbohydrate. Wheat. How many other food products can you name that are sources of carbohydrates? Courtesy, Ohio State Experiment Station.



## I. OCCURRENCE, CLASSIFICATION, AND STRUCTURE OF CARBOHYDRATES

### Occurrence and Importance

Carbohydrates, one of three great classes of foods, are very important from a physiological standpoint, since they include the sugars and the starches. In addition to starches and sugars, the term carbohydrate includes cellulose, which is the major constituent of the woody or fibrous part of all plants, and is the ultimate source of some of our fuel (wood, coal), much of our clothing (cotton, linen, rayon), and a large part of our building material (wood). In roots and seeds and in vegetables and unripe fruits, the carbohydrates occur as starch, but as fruits ripen the starch is converted into sugar.

### Composition and Classification:

Carbohydrates contain three tasteless elements: carbon, hydrogen, and oxygen, the last two elements, with but insignificant exceptions,\* being present in the same ratio as in water, namely two atoms of hydrogen to one of oxygen. It is for this reason that the general formula of most carbohydrates can be represented as  $C_n(H_2O)_n$ . Thus in the formula of sucrose (cane, beet sugar),  $C_{12}H_{22}O_{11}$ , the ratio of the atoms of hydrogen to the atoms of oxygen is 2 to 1, the same as in  $H_2O$ . As the name implies, carbohydrate means "hydrates of carbon." However, the name is somewhat misleading since the hydrogen and oxygen do not exist as water of hydration in a carbohydrate. Carbohydrates are best defined as polyhydroxy aldehydes, polyhydroxy ketones or substances which can be hydrolyzed to give these structures. This will be borne out later in the structures for simple sugars and in the study of the hydrolysis products from disaccharides and polysaccharides.

There are several ways of classifying the carbohydrates. In general they form two classes: those that are sweet, crystalline solids, called sugars, and those that are tasteless noncrystalline solids, called starches and celluloses. From their chemical behavior with water (hydrolysis), carbohydrates may be classified according to the number of saccharide ( $C_6H_{10}O_5$ ) groups in their molecules, the monosaccharides containing one, the disaccharides two, and polysaccharides three or more of these groups. The term saccharide

\* Acetic acid  $CH_3COOH$  and lactic acid  $CH_3CHOHCOOH$  contain H and O in the ratio as found in water but are not carbohydrates. Furthermore several compounds such as rhamnose  $C_6H_{12}O_5$  do not have their H to O in the ratio of 2:1 but are grouped with the carbohydrates on account of similarity in their properties.

## CLASSIFICATION OF IMPORTANT CARBOHYDRATES

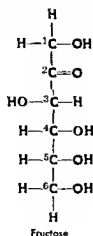
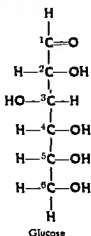
<i>Classification</i>	<i>Examples</i>	<i>Some Properties</i>
Monosaccharides ( $C_6H_{10}O_5$ ) $\cdot H_2O$ or $C_6H_{12}O_6$ Cannot be hydrolyzed	Glucose Fructose Galactose	Crystalline, sweet, very soluble, require no digestion
Disaccharides ( $C_6H_{10}O_5$ ) $_2 \cdot H_2O$ or $C_{12}H_{22}O_{11}$ Can be hydrolyzed	Sucrose Lactose Maltose	Crystalline, sweet, soluble, digestible
Polysaccharides ( $C_6H_{10}O_5$ ) $_n$ Can be hydrolyzed (Since the molecular weight is unknown $n$ refers to an unknown number of these groups)	Starch Dextrin Cellulose Glycogen	Amorphous, with little or no flavor, less soluble Vary in solubility and digestibility Form colloidal dispersions which cannot be dialyzed

means sweet and should not be confused with the term "saccharine," which is a coal tar compound that bears no relation to a carbohydrate (Saccharine is approximately 500 times as sweet as cane sugar, but it has no nutritive value, since it is not digestible and is eliminated from the body unaltered)

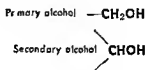
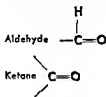
The monosaccharides are still further classified on the basis of the number of carbon atoms in the molecule, as pentoses,  $C_5H_{10}O_5$ , hexoses,  $C_6H_{12}O_6$ , etc., of which the hexoses are the most abundant and most important

**Structure:**

Following are the structural formulas for two important monosaccharides, glucose, an aldohexose, and fructose, a ketohexose



The structure for glucose reveals the aldehyde group at carbon number one. In the structure for fructose a ketone group appears at carbon number two. From these formulas it is evident that in the monosaccharide molecule all carbons are joined in one chain, and that the structure may be regarded as a polyhydric alcohol which contains either the aldehyde or the ketone group. Consequently the chemical behavior of a monosaccharide is due to the presence of the following groups



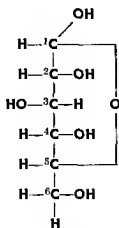
In order to distinguish between aldehyde and ketone types of monosaccharides the terms aldose and ketose are used, the "ose" signifying a sugar. Thus the name aldohexose represents a six carbon atom sugar with an aldehyde configuration.

The carbon atoms numbered 2, 3, 4, and 5 in the glucose molecule are called asymmetric (without symmetry) because each one has four unlike factors attached to it. Isomeric structures then become possible through a variation of the relative positions which the attached factors occupy in space. The glucose molecule pictured here is but one of sixteen aldohexoses. Chemists indicate this by writing the structure for ordinary glucose with the hydroxyl group attached to carbon number three placed on the left, while the hydroxyl groups on carbons two, four, and five are written on the right.

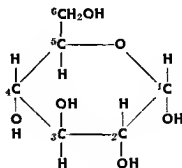
Some of the chemical reactions of glucose, as well as other sugars, suggest that the open chain structure with its free aldehyde (or ketone) group exists only to a small degree. Cyclic structures have therefore come into use for the sugars.

In the cyclic structures for glucose the free aldehyde group does not appear, it is, however, said to be potentially free. Undoubtedly in solution an equilibrium exists between the ring and the open chain forms, with the ring form predominating.

The disaccharide structure shows two molecules of monosaccharide linked together by the elimination of one molecule of water.

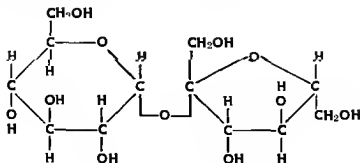


Fischer formula

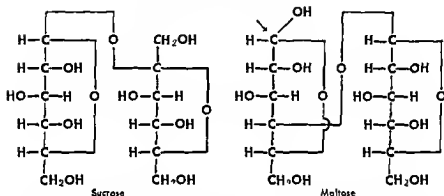
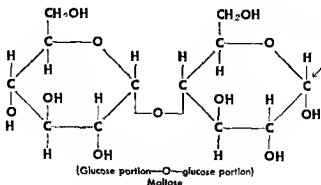


Haworth formula

to form an oxygen (ether) bridge. The resulting disaccharide may still have a potentially free aldehyde or ketone group, and if such is the case it will show the properties of the aldehyde or ketone, just as do glucose and fructose. There is one important disaccharide, namely, sucrose, which does not have any reducing properties. Evidence shows that for this sugar the aldehyde group of glucose and the ketone group of fructose have both been utilized in forming the new oxygen linkage, and hence both have been destroyed as reducing groups. In contrast to sucrose, the disaccharide maltose is a reducing sugar since it possesses a potentially free aldehyde group, indicated by the arrow in the following structures for this sugar. Lactose is very similar to maltose.



(Glucose part on—O—fructose part on)  
Sucrose



The polysaccharides have variable molecular weights with numerous carbon chains linked together through oxygen atoms. Like sucrose, the polysaccharides are nonreducing carbohydrates. They may be considered as composed of hexose molecules less one molecule of water for each hexose molecule present. The formula becomes  $(C_6H_{10}O_5)_n$ , where  $n$  refers to the number of  $C_6H_{10}O_5$  residues in the structure.

### SELF-TESTING QUESTIONS

1. What substances are included under the name of carbohydrates?
2. In what forms are carbohydrates stored up in plants?
3. Define carbohydrate from its atomic composition, from its characteristic groupings.
4. What is the distinction between saccharide and saccharine?
5. What is an aldose? a ketose?
6. To what are the reducing properties of sugar attributed?
7. What disaccharide does not have reducing properties?
8. How do the three classes of carbohydrates compare in their physical properties?

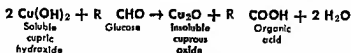
## II. CHEMICAL PROPERTIES OF CARBOHYDRATES

As has been mentioned the chemical behavior of a carbohydrate is determined by the presence of the aldehyde or ketone structure and the primary and secondary alcohol groups. With this in mind, and an understanding of the properties of such groups, the reactions of the carbohydrates are somewhat simplified.

### 1. Reducing Properties of Carbohydrates\*

The monosaccharides and the disaccharides, with the exception of sucrose, are good reducing compounds because of the presence of a free, or potentially free, aldehyde or ketone group. Sucrose, and the polysaccharides, however, show little or no reducing action with oxidizing agents, because of the absence of reducing groups. When these oxidation-reduction reactions once start the alcohol groups are then affected by oxidation. It is often important to discover if glucose is present in foods, or in such waste matter as the urine. Glucose is the only sugar of great physiological significance in the urine. Here, the presence of glucose indicates glycosuria, the chief symptom of diabetes. Since glucose sugar has a great affinity for oxygen, i. e., it has reducing properties on account of its aldehyde group, it is easy to make a test for this sugar. Benedict's and Fehling's solutions are the reagents very commonly used for this test. Benedict's solution, which is a modification of Fehling's solution, has many advantages over other solutions used to test for sugar in the urine. This solution is a permanent single solution, and, in contrast to Fehling's solution, is less alkaline and more sensitive to reducing sugars. Moreover, it is not affected by uric acid, creatinine, or chloroform, the latter compound being sometimes employed as a preservative for specimens of urine. Benedict's and Fehling's solutions both contain soluble cupric hydroxide. Either deep blue alkaline solution, if boiled with any solution containing glucose (an aldehyde sugar), is reduced to form a reddish yellow\* precipitate of cuprous oxide and an organic acid as explained in the following equation:

\* The yellow precipitate first formed is  $\text{CuOH}$  which on long boiling changes to red  $\text{Cu}_2\text{O}$ . Just a trace of yellow precipitate in the presence of blue cupric ions imparts a green color to the solution. If conditions are carefully controlled and Benedict's or Fehling's solutions are carefully prepared the test may be used as a quantitative method for the determination of a reducing sugar each solution being made of such a strength that a definite volume will be reduced to  $\text{Cu}_2\text{O}$  by exactly 0.05 Gm. of glucose. Fructose & hydroxy ketone differs from ordinary ketones by reducing Fehling's solution.

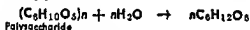


Milk sugar, or lactose, is also a reducing sugar, and consequently the urine of pregnant and nursing women will give the same test as glucose sugar. On the other hand, milk sugar does not ferment with yeast, as does glucose.

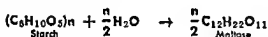
## 2. Hydrolysis of Carbohydrates

In the presence of certain nonoxidizing *dilute acids* like HCl or in the presence of certain *enzymes*† both the disaccharides and polysaccharides react with water to yield molecules of monosaccharides. If acid causes the change the final product is a monosaccharide, but with enzymes (amylases) the end product of the hydrolysis of a polysaccharide such as starch is the disaccharide, maltose.

### Hydrolysis by acids



### Hydrolysis by amylases



† Enzymes or ferments are catalysts produced by living organisms

## DIGESTION OF CARBOHYDRATES

Enzyme	Found in	Carbohydrates	End Product
Sucrase (invertase)	Intestine	Sucrose	Glucose and fructose
Maltase	Intestine	Maltose	Glucose
Lactase	Intestine	Lactose	Glucose and galactose
Salivary amylase (ptyalin)	Saliva (mouth)	Starch	Dextrin to maltose
Pancreatic amylase (amylotin)	Pancreas	Starch	Dextrin to maltose
Glycogenase	Liver	Glycogen (liver starch)	Glucose

In organic chemistry, this kind of a chemical decomposition involving water is called *hydrolysis*. In a previous chapter we learned (p 182) that hydrolysis is the reaction of a salt with water to form an acid and a base. Now in a broader sense, hydrolysis represents reactions of compounds other than salts with water.

The table on page 330 shows the hydrolytic changes in the carbohydrates as produced by the different enzymes in the body.

### 3 Fermentation of Carbohydrates

An interesting and characteristic property of the carbohydrates is that some of the sugars undergo fermentation with yeast. Fermentation is a term used for the decomposition of carbohydrates brought about by the lower organisms of life, namely, the *bacteria*, the *yeasts*, and the *molds*. When glucose ferments ethyl alcohol is produced.



Fig 2—Bacteria



Fig 3—Yeasts



Fig 4—Molds

All alcoholic beverages are the result of fermentation. Each beverage is the result of fermentation of the particular sugars formed from the grain or present in the fruit by a microorganism especially adapted for the purpose. For instance wine spoils when a certain microorganism is present. Pasteur first observed that wines soured in certain wine growing districts in France. He finally found the germ which caused the wine to sour, a discovery which led him to search for organisms as a possible cause of human or animal diseases. By heating the wine to a temperature of 60° C, on three successive days, he was able to destroy the germs without changing the character of the wine. This method long since has been called "pasteurization," and is now employed for the commercial pasteurization of milk.



Some fermentations produce acids, as when acetic acid is formed in the preparation of vinegar from apple juice, and commercial lactic acid from glucose, molasses or whey



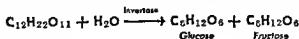
The disaccharides sucrose and maltose (lactose excepted) readily undergo alcoholic fermentation. Lactose does not show alcoholic fermentation, but will undergo acid fermentation to yield lactic acid. Acid fermentation of sucrose by a fungus is a commercial method of making citric acid.

Since fermentative bacteria are always found in the intestines, there will be a certain amount of acids and gases produced therein during the course of digestion. If the amount becomes excessive, the acids and gases may cause digestive disturbances. This may be partially overcome by carefully regulating the carbohydrates in the diet.

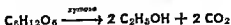


Fig. 5—Fermentation tube

The yeast cell, which produces fermentation, contains an enzyme called *zymase*. Actually zymase is a collection of enzymes. Zymase acts only on monosaccharides, but yeast contains a second enzyme, *invertase*, which is capable of hydrolyzing the disaccharide cane sugar into glucose and fructose just as an acid may hydrolyze it,



thus preparing it for the action of *zymase*

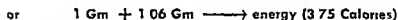
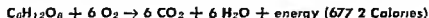


The activity of the zymase is conditioned by the presence of a number of substances, notably phosphates and a complex substance called "cozymase"

Starch, a polysaccharide, cannot be fermented by yeast, but certain enzymes in plant cells, as *diastase* in sprouting grains, and enzymes (ptyalin, amyllopsin) in the digestive juices, can change the starch into maltose. If the change from starch into maltose has been brought about by diastase, then *maltase*, a third enzyme of the yeast cell, can hydrolyze the maltose into glucose, which, in turn, can be fermented by zymase. Alcohol, then, may be considered as a product of the hydrolysis of starch into glucose, followed by the alcoholic fermentation of the glucose. It is from this source that a portion of the alcohol of commerce is obtained.

#### 4. Oxidation of Carbohydrates\*

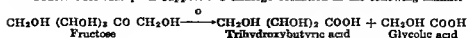
Sugars, sucrose\* excepted, readily undergo oxidation, the aldoses being easier to oxidize than the ketoses. Oxidation first starts with the aldehyde group, then with the primary alcohol groups, and finally with the secondary alcoholic groups, eventually to form carbon dioxide and water. Ketoses upon oxidation yield acids\*\* of lower molecular weights before finally being oxidized to carbon dioxide and water. By the time the carbohydrates reach the body cells they are converted into glucose,  $C_6H_{12}O_6$ . Glucose easily undergoes oxidation to form carbon dioxide and water with the release of energy amounting to about four Calories per gram.



There is no ash left, just the evolution of heat with the formation of carbon dioxide and water. Thus, the principal function of a carbohydrate in the body is to provide energy (about 1/6 of the calorie intake). As this energy is not always needed at the instant, animals generally store it in the form of fat or glycogen, while plants store it in the form of carbohydrates. Starch then may be

\* The fact that sucrose and the polysaccharides in contrast to the other carbohydrates scarcely show any reducing properties is due to the linkage between the reducing groups (aldehyde or ketone) of the monosaccharides composing them (p. 327).

\*\* Fructose for example is supposed to undergo oxidation in the following manner:



considered as a reserve supply of energy for plants. In animals carbohydrates are used almost as quickly as they are ingested, since they are quickly digested. In addition to the fact that carbohydrates are the source of practically all of our energy (p. 497), they also are used to some extent for building body fat (p. 512) and proteins.

The normal utilization of the carbohydrates takes place in the presence of *insulin*, an activating substance which is one of the hormones. Insulin is secreted by the pancreas and a lack of this body regulator leads to diabetes. However, it is now suspected that impairment of liver function is also a contributing factor in this disease.

### 5 Reactions with Alcohols—Esterification

Because of the presence of hydroxyl groups carbohydrates will form ethers and salts and will esterify with acids. The most important ester from a biochemical viewpoint is that formed by glucose reacting with phosphoric acid. This substance in large part changes into lactic acid and then into glycogen with liberation of energy for body purposes (p. 508).

### 6 Reduction of Carbohydrates

The monosaccharides and disaccharides (sucrose excepted) also undergo reduction with the absorption of energy and with the formation of products which the body uses to make into fat and other important substances. Just how the process goes on is not fully understood but we do know that it takes place since a carbohydrate diet is fattening (p. 511).

### 7 Formation of Osazones

In addition to the chemical properties previously stated the monosaccharides and disaccharides (sucrose excepted) react with the base phenylhydrazine  $C_6H_5NH-NH_2$  to form osazones in soluble compounds that vary in color, melting point and crystalline structure. The formation of osazones is a satisfactory method for the identification of a number of the sugars.

#### SELF-TESTING QUESTIONS

9. What is the significance of glucose in the urine?
10. Why does glucose react with Benedict's solution?
11. What are the advantages of Benedict's solution over Fehling's solution?
12. How can you make a test to differentiate between glucose and milk sugar?

13. What is hydrolysis in organic chemistry?
14. What are the hydrolytic products in the digestion of sucrose, maltose, lactose, starch, and glycogen?
15. What produces fermentation?
16. What is formed during fermentation of glucose?
17. What other kind of fermentation is there besides alcoholic fermentation?
18. Explain how starch may be changed into alcohol.
19. What is the function of zymase, invertase, and maltase?
20. What is the principal function of a carbohydrate?
21. How much heat is liberated upon oxidizing one gram of glucose?
22. How are carbohydrates stored in animals? in plants?

The following table summarizes the characteristic properties of the important carbohydrates:

	Carbo- hydrate	Physical and Physio- logical Properties			Chemical Properties				
		Amount Soluble in 100 Gm. of Water	Relative Sweet- ness Assuming Sucrose as 100	Dialyzes	Reduces Benedict's or Fehling's Solutions	Forms Yellow Osazones with Phenylhydraz- ine	Ferments with Yeast	Gives Color with Iodine	Hydrolyzes to
Monosaccharide	Glucose (dextrose)	80	74.3	+	+	+	+		
	Fructose (levulose)	+	173.3	+	+	+	+		
	Galactose	+	32.1	+	+	+	+		
Disaccharide	Sucrose (cane sugar)	198	100.0	+			+		Glucose + Fructose
	Lactose (milk sugar)	17	16.0	+	+	+			Glucose + Galactose
	Maltose (malt sugar)	+	32.5	+	+	+	+		Glucose
Polysaccharide	Starch	Colloidal						Blue	Glucose
	Dextrins	Colloidal	Slight			+	Following action of diastase	No color, blue or red	Glucose
	Glycogen	Colloidal						Reddish brown	Glucose
	Cellulose						By certain bacteria		Glucose

### III THE PRINCIPAL CARBOHYDRATES

#### The Monosaccharides ( $C_6H_{12}O_6$ )

The monosaccharides are the basic constituents of all carbohydrates. Disaccharides and polysaccharides are made up of monosaccharide groups. Not all monosaccharides (simple sugars) have nutritional significance, so we shall confine our study here to the three important hexoses as follows:

*Glucose* (also called *dextrose*, grape sugar, or corn sugar)

*Fructose* (also called *levulose*, or fruit sugar)

*Galactose*

GLUCOSE (an aldose), from the dietary viewpoint is the most important of the monosaccharides since it is the principal form in which a carbohydrate reaches the tissues for oxidation. In the free state glucose is commonly present with fructose in fruits, especially in the juice of ripe grapes (20 to 30 per cent), and it is the main constituent of honey. As it is directly absorbable, glucose is adaptable to conditions of impaired digestion and is a valuable food for babies and children. Honey, containing about 40 per cent each of glucose and fructose, quickly replaces in the blood and muscles the sugars that have been burned by strenuous exercise.

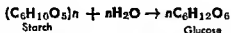


Analysis of Commercial Glucose

Water	18.48%
Dextrins	28.11%
Maltose	36.33%
Glucose	16.78%
Protein	0.5%
Ash	2.5%

Fig. 6—Commercial Glucose. Commercial glucose represents a product of incomplete hydrolysis. Why do the manufacturers prefer to call this product corn syrup? Courtesy A. E. Staley Mfg. Co.

Commercial glucose, a mixture of glucose, maltose, and dextrin, is obtained by the incomplete hydrolysis of corn starch (Fig. 6). The starch is heated under pressure with dilute hydrochloric acid (0.6 per cent), which serves as a catalytic agent. At the end of the process the acid is neutralized, the liquid is decolorized with bone black, and then concentrated to a thick syrup. Glucose is commonly known as corn syrup, a sweetening agent, much used in the prepara-



tion of jellies, table syrups, and candies. Its sweetness is surpassed only by fructose and sucrose.

Glucose (generally along with some sucrose) is also used to preserve foods because it deprives fermentative bacteria of water by plasmolysis. The more concentrated the sugar solution, the greater will be the osmotic pressure, and the consequent added protection against the growth of the bacteria which spoil food by fermentation.



Fig 7—Intravenous infusion. Introducing a glucose and saline solution into the vein. What is the purpose of the thermometer suspended in the antiseptic solution contained in the tall cylinder?

Corn syrup has become very popular as the carbohydrate used to modify cow's milk in infant feeding. In the hospital, highly refined glucose is used for intravenous infusions as a quick means of producing energy (Fig 7).

Glucose is found in the blood to the extent of about 0.1 per cent, although after meals this amount may be greatly increased, even so much that the blood cannot hold any more sugar (threshold point). In the latter case, glucose is excreted into the urine, causing a condition known as *glycosuria*. Such a condition is not patho-

logical, but is more of a protective device to keep the amount of sugar in the blood at a normal level. Insulin is supposed to control the utilization of glucose, as explained later.

Pure glucose is a crystalline solid, is fairly soluble (80 parts to 100 parts of water), and is sweet, but much less so than sucrose.

FRUCTOSE (a ketose) is very similar to glucose in properties and it occurs, as does glucose, particularly in many fruits from which it gets the name of fruit sugar. On a commercial basis it is largely obtained by the hydrolysis of inulin, a polysaccharide found in the Jerusalem artichoke.

Fructose is the sweetest of all of the common sugars. Because of its sweetness (nearly twice that of sucrose), great solubility, difficulty to crystallize from solution, and its ability to absorb moisture and consequently not dry out by complete crystallization, fructose has a decided advantage over other sugars in candy making. Such a sugar is useful in making chocolate centers, but the present price of fructose curtails its extensive use.

GALACTOSE, another monosaccharide that is similar to glucose in its chemistry, is mentioned here because during digestion lactose (milk sugar) is hydrolyzed to glucose and galactose. Galactose is also formed from blood glucose by the mammary glands. The presence of a complex form of galactose in nerve and brain tissue would indicate an important use in infant feeding. Also it is used as a liver function testing agent.

### SELF-TESTING QUESTIONS

- 23 Why is glucose the most important monosaccharide?
- 24 Where is glucose found?
- 25 Why is honey considered a valuable food?
- 26 How is commercial glucose made?
- 27 What is the hospital use of glucose?
- 28 What are the chief commercial uses of glucose?
- 29 What is glycosuria?
- 30 How does glucose compare in taste with cane sugar?
- 31 Enumerate four chemical properties of glucose.
- 32 Why is galactose of biological interest?

### The Disaccharides ( $C_{12}H_{22}O_{11}$ ):

These sugars, built up from two monosaccharide molecules minus a molecule of water, are of biochemical importance as food substances. They are

*Sucrose* (cane, or beet sugar)  
*Lactose* (milk sugar)  
*Maltose* (malt sugar)



Fig. B—Table Sugar. Sucrose or table sugar is the same substance whether obtained from sugar beets or sugar cane. What chemical changes are involved in photosynthesis to make plants stand between the race and starvation? *Courtesy, Sugar Research Foundation Inc.*

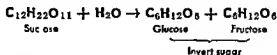
**SUCROSE:** This is ordinary sugar, obtained generally from sugar cane and sugar beets, although it does occur to some extent in honey and in the sap (maple) and tissues of many of our common plants (carrots, beets, etc.)

The refining of ordinary sugar consists in filtering the juice, precipitating the albuminous material, neutralizing the acids in the juice, evaporating the filtrate to the concentration where crystallization takes place, and separating the crystals from the mother liquor or molasses. Molasses is an important source of commercial ethanol as it readily undergoes alcoholic fermentation with yeast.

If heated carefully sucrose may be melted, but an increase in temperature (about  $200^{\circ}\text{C}.$ ) will partially decompose it into a brown amorphous substance called *caramel*. Caramel is much used as a flavor, as in making butterscotch pie, custards, or puddings. During caramelization at high temperature acrolein, an aldehyde, forms, which accounts for the sharp penetrating odor coming from



burned sugars spilled in a hot oven. Some caramel is used as a coloring substance in such food preparations as gravy, vinegar, and synthetic vanilla extract. Sucrose when boiled with water, and a small amount of an acid or an acid salt like cream of tartar to act as a catalytic agent, hydrolyzes according to the following equation:



The two sugars, glucose and fructose, collectively called *invert sugar* are used extensively in intravenous therapy. Invert sugar is sweeter than sucrose, and crystallizes with difficulty in water. Advantage of this latter property is taken in making fudge and butterscotch sauces for ice cream. In a similar way boiling sucrose with vinegar prevents taffy from "going to sugar." Because of its hygroscopic power, invert sugar is useful in keeping foods moist, a property used in keeping frostings, fondants, and other sugary coatings from drying out.

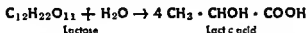
The alcoholic groups (—OH) of sucrose make possible the formation of salts. For instance the filtrate from a 50 per cent solution of sucrose and a small amount of calcium hydroxide to form calcium saccharate finds a use in making cream whip more easily.

Sucrose may be distinguished from the monosaccharides, and the disaccharides lactose and maltose, by the fact that sucrose does not respond to the test for the carbonyl group ( $=\text{C}=\text{O}$ ), i.e., it does not reduce Benedict's solution and does not form an osazone. This inability of sucrose to behave like an aldehyde or ketone sugar indicates that the characteristic properties of the aldehyde and ketone groupings have been destroyed in the union of the two molecules of hexose (p. 327). Sucrose, like glucose, undergoes alcoholic fermentation with yeast.\*

**LACTOSE (MILK SUGAR)** This sugar is present in the milk of all animals and during pregnancy it may be found in the urine. Cow's milk contains about 5 per cent of lactose, while human milk runs somewhat higher containing from 6 to 7 per cent. Lactose is not so sweet or so soluble in water as cane sugar. It is fortunate that lactose is less sweet than sucrose since this prevents milk from being nauseating and it also prevents babies from becoming accustomed

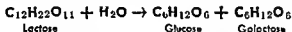
\* The inverting enzymes first hydrolyze sucrose and then the zymase enzymes ferment the invert sugar.

to having foods which are too sweet, a very important dietary measure when one wishes to make up a drink of high calorific content. The souring of milk is the result of the fermentation of lactose into lactic acid (lactic fermentation)

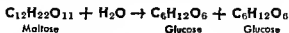


Not only does lactic acid precipitate casein in milk, but the rennin in the stomach also precipitates casein. Casein precipitated from cow's or goat's milk by rennin is used in the making of cheese. The liquid left, called whey, contains the milk sugar. Lactose sugar does not ferment with pure yeast, nor is it very soluble. The fact that lactose does not ferment so easily as the other sugars would indicate another importance in infant feeding, since it would allow less chance for intestinal disturbances. The presence of lactic acid in the intestine checks the growth of putrefactive bacteria, and since both lactose and lactic acid are present in buttermilk, it may be understood why buttermilk and many similar commercial preparations are popular foods.

Upon hydrolysis in the intestines, lactose yields glucose and galactose. The digestive enzyme lactase is the catalyst.



**MALTOSE (MALT SUGAR)** This sugar, especially abundant in germinating seeds, is formed from starch by the action of an enzyme, diastase, which exists in sprouting barley. An extract of sprouting barley, called malt extract, produces maltose from starch. In a similar way the enzyme *ptyalin* (salivary amylase) of the saliva and *amylapsin* (pancreatic amylase) of the pancreatic juices can change starch into maltose. Maltose, like lactose, is not so sweet as sucrose, and finds a wide use in making malted milk. With dextrin it forms many valuable patented foods. In the body maltose is hydrolyzed by the enzyme maltase of the intestine into two molecules of glucose.



**Malt sugar readily ferments with yeast**

## SELF-TESTING QUESTIONS

- 33 What are the sources of sucrose?
- 34 How is sucrose refined?
- 35 What is an important source of ethanol?
- 36 How is caramel made and for what is it used?
- 37 What is invert sugar and how does it differ in properties from sucrose?
- 38 How does sucrose differ from the monosaccharides and the other disaccharides in its chemical behavior?
- 39 Why does not sucrose show reducing properties?
- 40 How does the percentage of lactose differ in cow and human milk?
- 41 Why can it be considered fortunate that lactose is not so sweet as sucrose?
- 42 In what two ways may casein be precipitated?
- 43 What are the hydrolysis products of sucrose and of lactose?
- 44 How is maltose made?

The Polysaccharides ( $C_6H_{10}O_5$ )<sub>n</sub>

They include

*Starches*

*Dextrins*

*Glycogen* (animal starch)

*Celluloses* (vegetable fiber)

As a group (polysaccharoses), the polysaccharides are amorphous solids with little or no flavor, and they vary in their solubility and digestibility. Like most compounds of high molecular weight, they

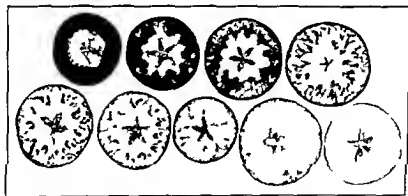
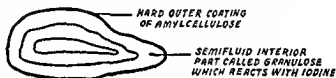


Fig 9—Ripening of Fruit Changes Starch to Sugar. As shown by the iodine test apples which were picked too early (when too immature) show a heavy amount of starch in all but the core area. Why are apples picked at about the stage represented in apple four (top row counting from the left)? Courtesy Division of Horticulture, Central Experimental Farm, Ottawa, Canada.

are not crystalline and form typical colloidal dispersions that are incapable of dialysis. Because of the absence of a free carbonyl group ( $=C=O$ ) the polysaccharides, like the disaccharide sucrose, do not have reducing properties or form osazones.

**STARCH** This is the principal form in which most plants store their food supply (potato 20 per cent, wheat 65 per cent, corn 65 per cent, rice 80 per cent). Starch is the cheapest, most plentiful and most important of our foods. Fruits as apples and bananas contain starch when green, but when ripe the starch has been hydrolyzed to glucose with an accompanying sweet taste. At the same time there is an apparent decrease in pectin as evidenced by the fact that unripe fruits produce firmer jellies than ripe fruits. On the other hand the changes that occur in sweet corn and peas are the exact opposite of those changes that take place in unripe

Fig. 10 — Starch Granule from Potato. How would you make a test for starch?

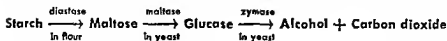


fruits, i. e., the sugar gradually changes to starch. Starch grains under the microscope show concentric rings of cellulose between which is a semifluid polysaccharide which gives a blue color with iodine solution. During cooking the moist heat swells and ruptures the hard partitions, thereby allowing the semifluid portion to be partially dissolved and more easily digested. It is for this reason that starchy foods are generally considered to be made more digestible by cooking. However, recent experiments have shown that all uncooked starches, potato starch excepted, digest as well as cooked starches, but that it takes longer to digest raw starches.

In the mouth, starch can be changed by ptyalin into maltose and dextrins, but the greater part is hydrolyzed by amyllopsin of the pancreatic juice to maltose, and then by maltase to glucose.

Boiled starch in neutral or faintly acid solutions upon being cooled forms a colloidal gel (starch paste) which gives a blue color with iodine solutions. The blue color vanishes on heating, but reappears on cooling. Boiling with dilute mineral acids gradually hydrolyzes starch to dextrin, maltose, and glucose, while cold dilute acids slowly produce the "soluble starch" that is used for laundry purposes.

Yeast will not ferment starch. However, in bread making, diastase in the flour hydrolyzes some of the starch into maltose, which is changed by maltase of the yeast into glucose. The glucose is then fermented by zymase of the yeast into  $\text{CO}_2$  and ethyl alcohol.



Starch and the other polysaccharides, unlike the monosaccharides and disaccharides, do not dialyze.



Fig. 11—Starch Foods. Which food pictured here likely is richest in starch?  
Courtesy, National Dairy Council.

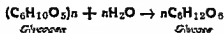
**DEXTRIN** This polysaccharide is a white amorphous substance formed by beating dry starch, and in a sense is a product intermediate between starch and sugar. In solution, dextrin is slightly sweet, and, with iodine solution usually gives a violet to reddish brown color, the larger dextrin molecules (erythrodextrin) giving the darkest colors. The very simple dextrin molecules (achrodextrin) give no color change with iodine. During hydrolysis of starch by enzymes or acids there is a decrease in molecular weight, and the following color changes with iodine take place

**Starch** → **Erythrodextrin** → **Achraodextrin** → **Maltose** → **Glucose**  
 blue                      red                      colorless                      colorless

Bread crust and toast especially Melba toast, owe their sweetness to dextrin. Since a solution of dextrin is sticky, it is often used as an adhesive. For example, the mucilage on the back of postage stamps is made of dextrin. In medicine, dextrin is used mainly for its adherence properties, and occasionally as an emulsifying agent (colloidal property). Also dextrin is used industrially to give smoothness to candy. The stickiness of corn syrup is mainly due to the dextrin present. Some dextrans slightly reduce Benedict's solution and all of them form osazones.

**GLYCOGEN** This is an animal starch, a carbohydrate reserve formed from blood sugar (p 514), and from a part of the protein and fat in the blood (pp 516 521 522)

Glycogen is present in all body cells particularly the muscle tissue and in the liver. Sometimes the liver contains as much as ten ounces of glycogen. That glycogen furnishes a reserve supply of energy needed by the tissues is shown by its rapid disappearance from the liver during sudden strain produced by fright or excess exercise.



Glycogen is somewhat soluble (unlike starch), forms an opalescent solution in water, and with iodine solution gives a red to brown (port wine) color. It does not reduce Benedict's solution, nor does it ferment with yeast or form an osazone.

Oysters and other shellfish contain as much as 9 per cent of glycogen and since liver always contains a large amount of glycogen, both of these foods should be carefully considered in the low carbohydrate diet of diabetic patients.

## SELF-TESTING QUESTIONS

- 45 How is starch digested?
- 46 What are the general properties of the polysaccharides?
- 47 What is the test for starch?
- 48 Why are starch foods cooked?
- 49 How is dextrin made?
- 50 What is the test for dextrin?
- 51 What are the medicinal uses of dextrin?
- 52 Where is glycogen found in the body?
- 53 From what is glycogen formed in the body?

## IV. CELLULOSE

## Physiological Uses of Cellulose

Industrially and economically cellulose is the most important carbohydrate. Although a polysaccharide it is not a nutrient for human consumption. It is the principal constituent of the cell walls of plants. Linen, cotton, hemp, and flax are chiefly cellulose. Cellulose is insoluble in water, and because the body has no enzymes capable of producing its hydrolysis it is very indigestible. However, herbivorous animals are able to decompose and use it as a food. Older people often need to eat the soft cellulose present in vegetables as it gives bulk and causes peristaltic action in the intestine. In this way it assists in preventing constipation. It is however, prohibited in spastic conditions of the intestines. A list of foods which help waste elimination is shown below.

## FOODS WHICH HELP WASTE ELIMINATION

---

<i>Apples</i>	<i>Cauliflower</i>	<i>Grapefruit</i>	<i>Pineapple</i>
<i>Apricots</i>	<i>Celery</i>	<i>Grapes</i>	<i>Plums</i>
<i>Asparagus</i>	<i>Cereals (whole grain preparations)</i>	<i>Honey</i>	<i>Prunes</i>
<i>Beets</i>	<i>Cranberries</i>	<i>Lettuce</i>	<i>Radishes</i>
<i>Bran</i>	<i>Cucumbers</i>	<i>Maltose</i>	<i>Raisins</i>
<i>Bread (bran whole-wheat graham)</i>	<i>Currants</i>	<i>Olive oil</i>	<i>Rutabagas</i>
<i>Brussels sprouts</i>	<i>Dates</i>	<i>Olives</i>	<i>Spinach and other greens</i>
<i>Buttermilk (yogurt or acidophilus)</i>	<i>Endive</i>	<i>Onions</i>	<i>Strawberries</i>
<i>Cabbage</i>	<i>Figs</i>	<i>Oranges</i>	<i>Tomatoes</i>
<i>Cantaloupe</i>	<i>Fruit juices, jellies or ices</i>	<i>Parsnips</i>	<i>Turnips</i>
<i>Carrots</i>		<i>Peaches</i>	<i>Watermelon</i>
		<i>Pears</i>	

---

**NOTE** Substances indicated by *italic type* are especially valuable for their minerals.

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When treated with a strong hydrolytic agent such as dilute sulfuric acid, cellulose yields glucose. It is for this reason that cotton goods are weakened by acids, as well as by alkalis (washing powders, soap). Although cellulose is the main product formed during the growth of plants, there are also present intermediate products, called *hemicelluloses*, which differ from the normal cellulose by being more readily hydrolyzed. The hydrolysis of hemicelluloses takes place very readily in the presence of an alkali, and explains why the addition of baking soda is more likely to soften young vegetables or fruits than old ones. Such an addition however may result in the destruction of vitamins. Cellulose differs from the other polysaccharides discussed by giving no color change with iodine.

**AGAR AGAR** This is a polysaccharide found in seaweed, and is of interest on account of its use in preparing solid culture media in bacteriology. Hydrolysis of agar agar produces galactose. Agar agar has little food value but when used medicinally it adsorbs large quantities of water, and for this reason is used to give bulk to the feces in order to overcome constipation.

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Note: The remainder of this chapter may  
be omitted where time must be saved.

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### Commercial Uses of Cellulose:

Through chemical changes a large number of valuable products are made from cellulose, the most important of which follow.

**CELLULOSE NITRATE (NITROCELLULOSE)** Since cellulose has alcoholic groups in its molecule it can react with acids to form esters, the most important of which are the nitrates and the acetates. Thus cellulose with nitric acid forms *cellulose nitrate* (pyroxylin), or, if three nitrate groups are substituted for as many hydroxyl groups *gun cotton is formed*. A solution of cellulose nitrate forms a transparent film. It is this property that makes these lower nitrates of cellulose suitable for preparing collodion, cellophane, celluloid, and certain lacquers. The higher nitrated forms are used for explosives. Pyroxylin used on certain fabrics makes artificial leather.

**CELLULOSE ACETATE** In decided contrast to cellulose nitrate, the ester cellulose acetate is nonexplosive and burns very slowly with the production of nontoxic fumes. As a consequence, cellulose



acetate finds an extensive use in the manufacture of "safety" (slow-burning) motion picture films, x-ray films, and "acetate" fabrics (Celanese).

**MERCERIZED COTTON:** When cotton cloth (cellulose) is treated with sodium hydroxide it shrinks and becomes tougher, and if the goods is under tension when thus treated, it will have a silky appearance. This material is called *mercerized cotton*.

**RAYON:** Cellulose, as wood fiber, when treated with sodium hydroxide, reacts with carbon disulfide, and yields cellulose xanthate, a yellow solid which readily dissolves in the sodium hydroxide solution to form water-soluble viscose. Upon forcing the heavy, yellow solution of viscose through minute tubes into dilute sulfuric acid, coagulation takes place with the formation of fine threads differing in composition but having a sheen somewhat like that of real silk. The manufactured cloth, called *rayon*, formerly was known as *artificial silk*.

**CELLOPHANE:** A cellulose product of great importance is cellophane, which is extensively used as a transparent wrapping material. The manufacture of cellophane differs from that of rayon



Fig. 12—Applying the Suture. Nylon, a synthetic fiber made from coal, air, and water, has a strength equal to silk, is elastic, and is insensitive to moisture. Why are nylon fibers suitable for surgical sutures? Courtesy, Bauer and Black

mainly in that the viscose is forced through a narrow slit and forms a sheet instead of a thread

**PAPER** Large quantities of cellulose such as fibers, and the cheaper grades of wood are used in the manufacture of paper. Linen and rag papers are no longer manufactured in quantity.

**ETHYL CELLULOSE, CARBOXYMETHYLCELLULOSE** In addition to cellulose showing the behavior of an alcohol in forming esters and cellulose xanthate, it will form ethers. One important ether is ethyl cellulose, a compound much used in paper sizing, printing inks, certain soaps, synthetic resins, and in adhesives. Another compound, carboxymethylcellulose (CMC), has similar uses.

### SELF-TESTING QUESTIONS

- 54 Why does cellulose form esters?
- 55 Name two important esters of cellulose.
- 56 What property of the low nitrates of cellulose makes them suitable for making collodion, cellophane, and certain lacquers?
- 57 What is artificial leather?
- 58 What are the advantages of cellulose acetate over cellulose nitrate in motion picture films?
- 59 How is mercerized cotton made and how does it differ in properties from ordinary cotton?
- 60 How is rayon made?
- 61 From what can paper be made?

### SUGGESTED ACTIVITIES

#### I THOUGHT-PROVOKING QUESTIONS

- 1 What is the initial source of all carbohydrates?
- 2 Discuss the possible various uses of saccharine.
- 3 How can you suggest a partial elimination of intestinal fermentation?
- 4 In what way is knowledge of the pH value of commercial glucose (corn syrup) of great importance in the manufacture of crystal line candies?
- 5 Why is maltose considered to be a valuable food for infant feeding?
- 6 When the skin of bananas shows signs of darkening why are the bananas considered more digestible?
- 7 Discuss the usefulness of fermentation in the home and in industry.
- 8 Account for the fact that a teaspoonful of vinegar beaten into boiled frosting when flavoring is added will keep the frosting from being brittle and breaking when cut.
- 9 How do you account for the use of cream of tartar in making fondant (a kind of candy)? The use of starch in corn starch puddings?
- 10 How may you account for agar, a dried gel being used like cellulose to relieve constipation?

- 11 As the carbohydrate molecules become larger and more complex in structure how are their properties changed?
- 12 How may the sweet taste of a solution containing sucrose be increased?
- 13 Why is it that young vegetables but not old ones, can be made more tender by boiling in the presence of baking soda?
- 14 Compare and contrast in tabular form the properties of the polysaccharides, paying particular attention to taste, solubility, hydrolysis, and the iodine test
- 15 What are the medicinal values of lactose?
- 16 How does the digestion of the disaccharides and polysaccharides by enzymes differ from hydrolysis produced by dilute nonoxidizing acids?

## II VOCABULARY TESTING OF NEW TERMS

carbohydrate	disaccharide	sldose
saccharide	fermentation	ketose
polysaccharide	alimentary glycosuria	asymmetric
monosaccharide	hydrolysis	hemicellulose

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Industrial Uses for Cellulose
- 2 Insulin to the Rescue of the Diabetic
- 3 Sugars in Nutrition
- 4 Natural Fibers vs Synthetic Fibers

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on page 720

## ANIMAL AND VEGETABLE FATS AND OILS

## CHAPTER OUTLINE

- |  |   |
|--|---|
| <p>I FATS AND OILS</p> <p>(a) General remarks</p> <p>(b) Occurrence of fats and oils</p> <p>II COMPOSITION AND NATURE</p> <p>(a) <i>Glycerides of fatty acids</i></p> <p>(b) Consistency of fats</p> <p>(c) Hydrogenation of fats</p> <p>III PROPERTIES OF FATS</p> <p>(a) Physical properties</p> <p>1 Greasy feeling</p> <p>2 Color</p> <p>3 Melting point</p> <p>4 Specific gravity</p> <p>5 Solubility</p> <p>6 Emulsification</p> | <p>(b) Chemical properties</p> <p>1 Hydrolyze</p> <p>2 Saponify</p> <p>Soap</p> <p>Varieties of soap</p> <p>Hymolal salts</p> <p>3 Assume a rancidity</p> <p>4 Decompose when heated</p> <p>5 Undergo oxidation</p> <p>IV PHYSIOLOGICAL IMPORTANCE OF FATS</p> <p>(a) Function in the body</p> <p>(b) Behavior in the body</p> <p>(c) Assimilation of fats</p> <p>V OTHER LIPIDS</p> <p>(a) Some complex and derived lipids</p> |
|--|---|

## I. FATS AND OILS

## General Remarks:

The animal and vegetable fats and oils make up a major division of a class of compounds of natural occurrence called *lipids*. The following classification has been suggested

- (1) *Simple lipids* These are esters of the fatty acids with various alcohols (a) Animal and vegetable fats and oils (b) Waxes
- (2) *Complex or compound lipids* Made up of esters of fatty acids which contain groups in addition to those found in the simple lipids (a) Phospholipids (b) Glycolipids
- (3) *Derived lipids* Hydrolytic products formed from simple and complex lipids (a) Sterols (b) High molecular weight fatty acids

The lipids have the common characteristic of water insolubility. They are, however, soluble in the so called fat solvents of which ether, chloroform, and carbon tetrachloride are representative.

The major portion of this chapter is devoted to a study of those simple lipids which are known collectively as the animal and vegetable fats and oils. These constitute one of the three major classes of foodstuffs.

### Occurrence of Fats and Oils:

Fats are widely distributed among both the animals and plants. In animal organisms, especially in the higher animals, fats are found in all *tissues*, between the muscles, around all *organs*, in bone marrow (96 per cent) and in very large amounts in adipose (fatty) tissue that is directly under the skin.

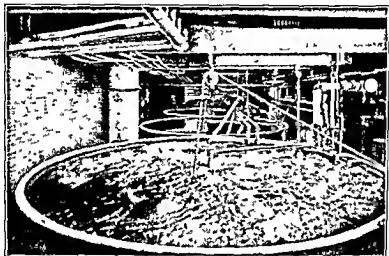


Fig. 1—A Seething Mass of Soap. Soap in the making. Does any form of soap appear in digestion? Courtesy, Swift & Company.

*Tallow* from cattle, sheep, and horses; *lard* from the fat surrounding the interior parts of the body (entrails); *suet* or the hard fat particularly about the kidneys; and *butter* from milk are our most important animal fats. In plant organisms, liquid fats called "oils" are found in the *seeds* (embryo), *roots*, and *fruits*. Vegetable fats occur in abundance in cottonseed oil (Wesson), linseed oil, palm oil, olive oil, coconut oil, peanut oil, corn oil (Mazola), and many others. The seeds of cereals are usually low in fat content since starch takes the place of fat in the composition of such seeds.

Vegetable fats (mostly soybean, cottonseed, coconut, and peanut oils) are used for preparing butter substitutes, called *margarines*. Following hydrogenation (p 356) the fats are churned with pasteurized, skimmed milk. Addition of butter flavor (butyrin), vitamins A and D, salt and coloring dye gives a food which compares

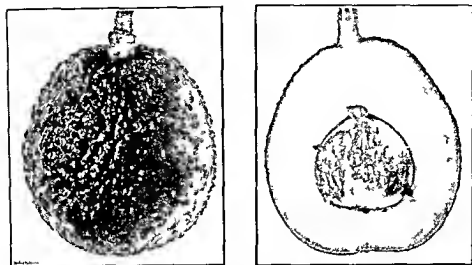


Fig 2—Avocado Fruit is a Rich Source of Vegetable Fat. The fat content of the avocado is as high as 50 per cent. How does the avocado compare in caloric value with other fruits? Courtesy Agricultural Experiment Station, University of Florida.

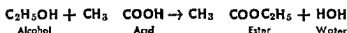
well with butter in odor, taste and food value. Today the production of oleomargarines exceeds that of butter.

## II. COMPOSITION AND NATURE OF FATS

Fats contain the same three elements as carbohydrates, namely, carbon, hydrogen and oxygen. However, the hydrogen and oxygen are not present in the same proportion as in water, and the relative amount of oxygen in fats is much smaller than that occurring in carbohydrates. The significance of this relatively small amount of oxygen is pointed out later.

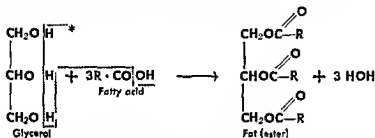
### Glycerides of Fatty Acids

It may be recalled that an ester is the result of an alcohol reacting with an acid.

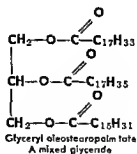
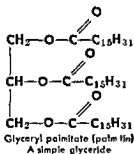


Fats are also esters and may be considered to have been formed by glycerol, an alcohol reacting with fatty acids of high molecular weight. The formula  $\text{C}_3\text{H}_5(\text{OH})_3$ , for glycerol shows that three hydroxyl groups may function in the formation of a fat, and since

the fatty acids are monobasic, that is, each acid contains one carboxyl group,  $\text{—COOH}$ , it follows that one molecule of glycerol will require three molecules of fatty acid to form a natural fat. If we use  $R$  as the general symbol for the hydrocarbon radical or residue, and use the formula  $R \cdot \text{COOH}$  to represent any monobasic acid, the relationship between glycerol and the fatty acids to form fats may be shown by the following equation,



In the simple glycerides (esters of glycerol) the three fatty acid residues are the same. If two or three kinds of fatty acid residues are present the glyceride is termed mixed.



In illustrating the general chemical characteristics of fats it is a practice to use the simple glyceride structure. However, it is to be noted that for the most part the *natural animal fats and vegetable oils are mixtures of mixed glycerides*.

The fatty acids which are most frequently found in the glycerides of fats and oils are butyric, palmitic, stearic, and oleic acids. The formulas for these acids and their glyceryl esters are included in the following table.

\* Evidence for this type of cleavage in contrast to the usual behavior of acids has resulted from the use of the heavy isotope of oxygen as a tagged atom.

**FATS DERIVATIVES OF GLYCEROL AND FATTY ACIDS**  
**TYPE FORMULA,  $C_3H_5(OOC R)_3$**

<i>Fatty Acid</i>	<i>Formula of Fatty Acid</i>	<i>Formula of Ester</i>	<i>Name of Fat</i>	<i>Occurrence of Fat</i>
<b>Saturated</b>				
Butyric	$C_4H_8O_2$ Series $C_3H_7COOH$	$C_3H_5(OOC C_3H_7)_3$	Glyceryl butyrate or butyrin*	Butter
Palmitic	$C_{15}H_{31}COOH$	$C_3H_5(OOC C_{15}H_{31})_3$	Glyceryl palmitate or palmitin	Palm oil lard
Stearic	$C_{17}H_{33}COOH$	$C_3H_5(OOC C_{17}H_{33})_3$	Glyceryl stearate or stearin	Tallow
<b>Unsaturated</b>				
Oleic	$C_nH_{2n-2}O_2$ Series (one double bond) $C_{17}H_{33}COOH$	$C_3H_5(OOC C_{17}H_{33})_3$	Glyceryl oleate or olein	Olive oil
Linoleic	$C_nH_{2n-4}O_2$ Series (two double bonds) $C_{17}H_{31}COOH$	$C_3H_5(OOC C_{17}H_{31})_3$	Glyceryl linoleate or linolein	Corn oil
Linolenic	$C_nH_{2n-6}O_2$ (three double bonds)	$C_3H_5(OOC_{17}H_{29})_3$	Glyceryl linolenate	Linseed oil

\* The name of the ester is derived from the name of its acid by using the suffix *in* for the final *ic* of the acid

Some additional unsaturated fatty acids of interest are linoleic acid in cod liver oil, ricinoleic acid in castor oil, and chaulmoogric acid, a cyclic fatty acid, in chaulmoogra oil. The ethyl ester of the latter acid was formerly used in the treatment of leprosy.

### Consistency of Fats

All natural fats are mixtures of glyceryl esters, and their consistency depends largely upon the various glycerides that are present. For instance, olein, the glyceride of unsaturated oleic acid, is a liquid to  $-6^\circ C$ , while palmitin and stearin, the glycerides of saturated fatty acids, are solids up to  $65.5^\circ C$  and  $71.6^\circ C$  respectively. In other words, saturated fats are solids.



The difference in the relative amount of olein (unsaturated fat) will determine whether a fat is a solid, semisolid, or a liquid (oil\*) at ordinary temperatures. Thus olive oil with about 95 per cent olein is a liquid, while animal fats with less olein and a larger percentage of the saturated fats, palmitin and stearin, are solids. Mutton fat has a little olein, beef fat somewhat more, while pork fat contains considerable olein (65 per cent) and is of a much greasier consistency (Fig. 3). It is due to the relatively high amount



Fig 3—Fat in Ham and Bacon. Why is pork fat greasier than most animal fats? Courtesy, U S Dept of Agriculture

of olein that the fat of cold blooded animals remains fluid at temperatures at which the fat of warm-blooded animals solidifies. Human fat with 70 to 80 per cent of olein, about 15 per cent of palmitin, and 5 per cent of stearin melts between  $20^{\circ}\text{C.}$  and  $25^{\circ}\text{C.}$ , and consequently is always a liquid at body temperature ( $37^{\circ}\text{C.}$ ).

### Hydrogenation of Fats:

From the previous paragraph, it is evident that at ordinary temperatures ( $20^{\circ}\text{C.}$ ) vegetable fats contain a larger proportion of olein, and are in the liquid state, while animal fats with less of the olein and more of the palmitin and stearin are solids. By comparing the formulas of atearic acid and oleic acid or their esters, it is noticeable that olein differs from stearin by containing six less hydrogen atoms per molecule, and that oleic acid has two less

\* In general, the word oil refers to any greasy feeling substance such as the natural fats as well as to substances not chemically related to the natural fats, such as mixtures of hydrocarbons (mineral oils), and to cyclic compounds of plant origin (oil of wintergreen, oil of lemon). It is customary to use the term fat when the substance is a solid at  $20^{\circ}\text{C.}$ , and if a liquid at that temperature to regard it as an oil.

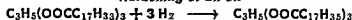


Fig 4—Hydrogenation of Vegetable Oils. Hydrogenation changes cottonseed oil into Crisco, and coconut and peanut oil into butter substitutes (nut margarine). What makes this reaction possible? Courtesy, Procter & Gamble Co

Acids	Ester
Stearic, $C_{17}H_{35} \cdot COOH$	Stearin, $C_3H_5(OOC \cdot C_{17}H_{35})_3$
Oleic, $C_{17}H_{33} \cdot COOH$	Olein, $C_3H_5(OOC \cdot C_{17}H_{33})_3$

hydrogen atoms than stearic acid. A similar difference of two less hydrogen atoms between ethane  $C_2H_6$  and ethylene  $C_2H_4$  was explained (p. 270) by assuming that the carbon atoms in ethylene have a double bond between them. This implies then that olein, like ethylene, is an unsaturated compound, that it contains a double bond, and is therefore capable of forming addition products. From this it is possible to understand how the addition of hydrogen atoms may convert liquid fats (unsaturated) into solid fats (saturated). Such a change of olein to stearin is accomplished by heating olein under pressure (225 lbs at  $180^\circ C.$ ) with hydrogen in the presence of a catalyst (finely divided nickel).

## Hardening of an oil



Olein (M.P. = -6°)  
Unsaturated fat (liquid)

Stearin (M.P. = 71.6°)  
Saturated fat (solid)

This reaction, known as **hydrogenation**, makes possible the manufacture of edible lard substitutes such as Crisco and Spry from cottonseed oil and other vegetable oils. The hydrogenated oils are particularly well adapted for deep fat frying. In the commercial hydrogenation of vegetable oils not all of the unsaturated content is converted to saturated, to do this would give a product too hard and brittle for use as a shortening in cooking. Today's shortenings are hydrogenated only sufficiently to eliminate the more highly unsaturated molecules which are responsible for poor keeping quality. Hence the resultant product, a soft solid, contains a considerable proportion of unsaturated glyceride.

It is because of unsaturation that certain fats absorb odors. Lard, for example, quickly absorbs an odor from frying fish, and butter absorbs odors from bananas and onions. This property of

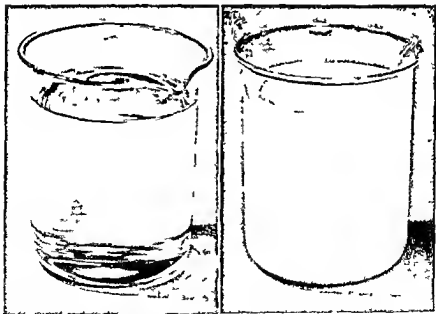


Fig 5—Hydrogenation. The hydrogenation of the vegetable oil pictured on the left gives the soft solid shown on the right. Does this solid contain any unsaturates? Courtesy, Procter & Gamble Co

absorption on the part of unsaturated fats is used to commercial advantage in extracting valuable perfumes, as rose oil from roses

In general it is to be remembered that unsaturated fats, in contrast to the saturated ones, are liquids. Like the unsaturated hydrocarbons the unsaturated glycerides form addition products at the double bonds, the most important of these being the addition of hydrogen

### SELF-TESTING QUESTIONS

- 1 What is the principal function of a fat?
- 2 Where are the fats found in animals and in plants?
- 3 Name four important animal fats
- 4 How is oleomargarine made?
- 5 What is a fat chemically?
- 6 Name the three most common fatty acids entering into the composition of natural fats
- 7 How do you account for the difference in the consistency of fats?
- 8 Why are some fats greasier than others?
- 9 How do the fats of the cold blooded animals differ from those of warm blooded animals in composition?
- 10 What is an unsaturated fat?
- 11 How is hydrogenation accomplished? What is the advantage of hydrogenation?

### III. PROPERTIES OF FATS

#### Physical Properties of Fats:

Even though fats vary in their consistency they bear a much closer resemblance to each other in their physical properties than they do in their chemical behavior. As a group, they show the following similarities

**GREASY FEELING** Fats are characterized by having a slippery, greasy feeling, and when in contact with many substances, penetrate them and produce grease spots. On paper, a grease spot becomes translucent, which serves as a simple physical test for a fat.

**COLOR** Fats and oils when pure are colorless, odorless, and tasteless, but when obtained in the natural form they may range in color from a yellow to a red. Natural oils generally are of a yellowish color because of the presence of a yellow fat soluble pigment. However, some vegetable oils, like olive oil, may have a green color due to the presence of the green pigment chlorophyll. Natural fats impart flavor to foods and make them more palatable. The taste of butter is in part due to the compounds produced by bacteria during the ripening of the cream.

**MELTING POINT** Since a fat is a mixture of glycerides of different fatty acids the melting point is not very sharp a low melting point indicating the presence of glycerides of unsaturated fatty acids

**SPECIFIC GRAVITY** Fats are lighter than water, their specific gravity being fairly uniform (0.86) in solid fats, but showing a greater variation in liquid fats (0.91 to 0.94)

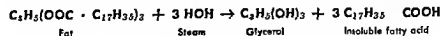
**SOLUBILITY** With such a small amount of oxygen in proportion to the large amount of carbon and hydrogen, fats closely resemble the higher hydrocarbons in their waxy nature, solubility, and in activity. The most characteristic physical property of those fats formed from the higher fatty acids is that they are readily soluble in ether, chloroform, carbon tetrachloride, gasoline, and boiling alcohol, but are insoluble in water. However, butyrim and other glycerides of the lower fatty acids are very slightly soluble in water. Fats are also soluble in each other. Of the fat solvents used for removing grease stains carbon tetrachloride (Carbona) and trichloroethylene are the easiest since they are not flammable (p. 278)

**EMULSIFICATION** With water, fats give an emulsion only after vigorous and prolonged shaking. The emulsion, however, is only temporary unless some colloidal substance such as soap, dextrin, or albumin is present. Then the colloids form a film on the surface of the tiny, dispersed fat globules and prevent them from running together to form larger globules of fat that ordinarily would separate out on top of water. An emulsion of oil suspended in this way in water has a milky appearance. Emulsification of fats in the intestines, a very important function of the bile, is of the greatest physiological importance since only in that condition are fats digested in the intestines. Furthermore, the fat that is carried by the blood to the cells is in the form of an emulsion.

### Chemical Properties of Fats

Although the chemical properties of the fats are few, still they are of decided interest and importance as may be noticed from the following

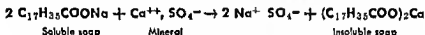
**1. FATS HYDROLYZE** The most important and characteristic reaction of fats is hydrolysis, since by this reaction fats are split up again into glycerol and fatty acids



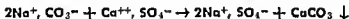
This reaction is important because all fats in the course of digestion



used in soap making is sodium hydroxide solid or hard soaps are formed, but if potassium hydroxide is used, semiliquid or soft soaps are made. Only these two metallic soaps are soluble in water and hence are the only ones that have any practical value in making lather for cleansing purposes. The glycerol formed in the preparation of soap is left in many commercial soaps as it has beneficial action on the skin and makes the soap transparent. However, dissolved soap (colloid) may be salted out from a soap solution by adding common salt, and the glycerol separated from the spent lye solution by distillation with steam. This precipitating action of salt water helps us understand one of the difficulties in obtaining a lather with sea water. On the other hand, when a soluble soap is used in hard water a chemical reaction takes place between the soluble soap and the minerals (p. 82) in the water to form an insoluble curdy precipitate of calcium and magnesium soap.



Since soap is used up in precipitating the calcium ions, a suds will not form until the calcium ions are removed. This explains why hard water is first softened by the addition of some cheap softening agent, such as washing soda (sodium carbonate), trisodium phosphate, or borax (p. 84). The calcium or magnesium ions are precipitated as insoluble carbonates, phosphates, or borates.



If sufficient soap is used, hard water will become soft, but as a softening agent soap is expensive. A further difficulty with hard water is that the sticky precipitate of insoluble soaps adheres to objects and is difficult to remove.

### Varieties of Soap

*Scouring Soaps* These are largely abrasive material, as fine sand, pumice, and infusorial earth held together by about 10 per cent of soap.

*Green Soap* This soap used in the hospitals is a soluble soft soap in alcohol, molded and dried.

*Germicidal or Medicated Soaps* These types (carbolic, Lysol, mercuric chloride) frequently have an irritating effect on the skin, and it is questionable whether they are as serviceable as claimed. Soaps containing hexachlorophene (Gamophen, Dysept, pHiso-hex)



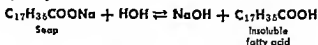
Fig 7—The Scrub Up To prevent infection strict asepsis must be practiced in hospitals. One drop of soap to one thousand drops of water will kill germs which cause many diseases. What are some of these diseases? Courtesy *Monsanto Magazine* Monsanto Chemical Company

are gaining in popularity as surgical scrub up soaps and toilet soaps, because they not only have pronounced bactericidal effects, but also are nonirritating. Ordinary lather made in washing the hands with any soap has considerable germicidal properties, as the lather itself is quite effective against all germs except the typhoid germ and the staphylococcus organism.\*

\*The germicidal action of soaps on such organisms as the streptococcus meningococcus gonococcus pneumococcus cholera and diphtheria bacillus is due primarily to the colloidal properties of the soap, the ability of the soap solution to lower surface tension, the temperature of the soap solution, the absence of the foreign material (albuminous) which interferes with the germicidal action, the diffusible or dialyzing power and the fatty acids present. In using soap in pure water the soap first dissolves and then partially hydrolyzes. Diano F A, Germicidal Value of Pure Soap. *Medical Review of Reviews*, Aug., 1934.



In using soap in pure water the soap first dissolves and then partially hydrolyzes



The fatty acids do not precipitate but stay in a colloidal condition. Soap solution, then, is really an *alkaline colloidal dispersion* and its



Fig 8—Testing Soap Effect on Skin. Women here soak their left arms in one soap solution and right arms in a second soap solution. After a measured interval the forearms and hands are examined to compare the effect of various soaps on the skin. Why are some soaps irritating to the skin? Courtesy Procter & Gamble Co.

cleansing power is due to the fact that when soap is rubbed upon the skin or other surfaces the colloidal particles pick up (adsorb) the dirt, and transfer it to the films that surround the air bubbles which compose the suds or foam. Any oily substances present are broken up by the rubbing to form minute droplets that become surrounded with films of soap to form a stable emulsion which is washed away. The cleansing power of a soap suspension is due to its *adsorbing* and *emulsifying* powers. The most important use of soap is to wash and yet not irritate the skin. Good hand soaps contain no free alkali to irritate the skin, the word "free" meaning any excess sodium hydroxide not used in the saponification. However, many cheaply made soaps contain sufficient free alkali to irritate the skin and to have a deteriorating effect upon silk, wool, and linen. Another point to remember is that the price paid for a soap does not guarantee its quality, since price depends to some degree upon the perfume and pigments added. Some of our cheap toilet soaps with no color or perfume may be even better than some of the more expensive brands.

**Floating Soaps.** These contain air beaten into them while in a pasty condition.

**Washing Powders.** These powders contain the water softeners (trisodium phosphate, sodium carbonate, borax, or sodium hexametaphosphate) and soap. The mixture is melted, dried, and then pulverized.

**Yellow Laundry Soap.** This type of soap usually contains the "filler" rosin, and an excess of sodium hydroxide (lye), a very undesirable ingredient in hand soaps. Such soaps have strong cleansing properties.

**Zinc Stearate.** This insoluble soap is a white dusting powder of importance for babies in that it has antiseptic properties and does not adsorb water like other powders do. However, since the dust of zinc stearate is irritating to the mucous membranes, care should be exercised when using it.

**Another Type of Detergent (Hymolal Salts).** Research in applied chemistry has produced a new type of detergent (Dreft, Drene) from higher alcohols, sulfuric acid, and caustic soda. The interesting thing about these salts is that they overcome two basic weaknesses of soap by not forming insoluble salts with calcium, magnesium or iron ions, and not leaving a soap film on clothes or dishes being washed. They produce an excellent lather even in hard



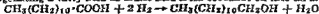
Fig. 9—Synthetic detergent at left produces suds in hard water while ordinary soap at the right forms insoluble curds. The value of detergents is limited to what two main facts? Courtesy, Du Pont Co.

water.\* For this reason these detergents are used in dentifrices and shampoos, and because they do not form alkaline solutions as do soaps they are fine for washing delicate fabrics which ordinarily might be injured by soap.

3. **FATS BECOME RANCID:** Upon long exposure to air, many unsaturated fats turn yellow, acquire an unpleasant taste, and develop free fatty acids to become rancid, a general term referring to any

\* These new detergents, called *hymtolal salts*, are made as follows:

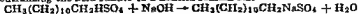
I. Hydrogenating a fatty acid as lauric acid from coconut oil into an alcohol



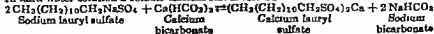
II. Sulfonating the alcohol into an acid sulfate



III. Neutralizing the acid sulfate to a neutral sodium salt



In hard water solution a soluble calcium salt is formed



Sodium lauryl sulfate

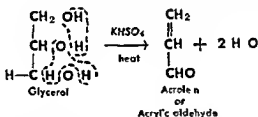
Calcium  
bicarbonate

Calcium lauryl  
sulfate

Sodium  
bicarbonate

objectionable odor or taste. This rancidity is the result of a *hydrolytic change* with the production of unpleasant smelling volatile fatty acids, and of the *oxidation* of unsaturated fatty acids with the formation of volatile aldehydes, shorter chained acids, and ketones. Rancidity, as in butter, not only may be due to exposure to air with the development of butyric acid, but also may be due to bacterial action upon impurities present. Since many foods such as bacon, cookies, peanuts, and potato chips are rich in fats, it becomes important to know how to prevent fats from becoming rancid. Experiment has shown that the acid formed during hydrolysis tends to act as a catalyzer in speeding up the reaction, also that the catalytic action of enzymes present is affected by temperature. Since both hydrolysis and enzyme action are relatively decreased by lowering the temperature, fats and foods rich in fat should be kept in a cool condition.

**4 FATS DECOMPOSE WHEN HEATED—ACROLEIN TEST** When fats are strongly heated ( $300^{\circ}\text{C}$ ), either alone, as in frying, or in the presence of a dehydrating agent like potassium hydrogen sulfate, they undergo hydrolysis. The glycerol which is released then undergoes dehydration to form acrolein, an unsaturated aldehyde.

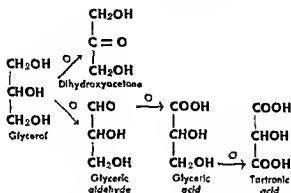


The presence of acrolein is recognized by its irritating effect on the mucous membranes of the eyes, nose, and throat, and by its acrid odor where grease has caught fire, or when meats have been broiled or roasted at too high a temperature.

As the glycerol radical is a part of all common fats, this formation of acrolein may be used as a standard chemical test for fats and glycerol.

**5 FATS UNDERGO OXIDATION** Fats are composed of hydrogen, carbon, and oxygen and like the carbohydrates yield carbon dioxide and water when completely oxidized. Since glycerol is a common constituent of all fats, and is a trihydric alcohol, the oxidation reactions of fats and oils show all the chemical reactions

of the primary and secondary alcohols. Some of the intermediate oxidation products are shown in the following diagram



As mentioned in the chapter on Oxygen, oxidation of fats in the body is accomplished at comparatively low temperatures because of the presence of certain catalytic agents. At the proper kindling temperature fats and oils burn. In fact, fats are frequently used commercially as a source of heat and light. Because of the greater chemical activity of unsaturated compounds, unsaturated fats at ordinary temperatures, even in the absence of a catalyzer, on exposure to air slowly combine with oxygen. This process, called auto oxidation, is involved in rancidity of fats, drying of oil paints or varnishes and in the fat changes in body cells.

### SELF-TESTING QUESTIONS

- 12 In what five important ways are fats similar in their physical properties?
- 13 What is a simple physical test for a fat?
- 14 Name five solvents for fats. What fats show a very slight solubility in water?
- 15 How do colloids make permanent emulsions?
- 16 Why is emulsification of great physiological importance?
- 17 What are the products of hydrolysis of fats?
- 18 What causes hydrolysis of fats in the body?
- 19 What is saponification?
- 20 Name two soluble soaps.
- 21 What is a soap?
- 22 How may soap and glycerin be separated?
- 23 What chemical reaction takes place when soap is dissolved in hard water?

- 24 How are the following soaps made green soap, scouring soap, germicidal soap, floating soap, washing powder, yellow laundry soap?
- 25 How do you account for the germicidal properties of ordinary lather?
- 26 To what two factors are the cleansing properties of soap due?
- 27 How do you account for some fats being colored and having a rancid odor?
- 28 What is a chemical test for a fat?
- 29 How does burnt fatty food affect digestion?
- 30 How do you account for oxidation of fat in the body at such a low temperature?

#### IV. PHYSIOLOGICAL IMPORTANCE OF FATS

##### Function of Fats in the Body:

From a physiological standpoint the fats are of great importance in the following ways

**AS A FUEL** Fats are heat producers, and for this reason they have a greater part in the diet during the winter than they do during the summer. The Eskimos in the far north consume large amounts of fats because they need the heat produced. Fats are very poor in oxygen, but rich in carbon and hydrogen. Consequently fats possess a large amount of latent chemical energy, and take up much oxygen to release correspondingly large quantities of heat. Since one of the important functions of foods is to keep the body at a temperature which is ordinarily above that of the air, fats take first rank among all foods in this respect, and therefore are extremely helpful in preserving animal life.

It is interesting to note again that 1 Gm. of fat produces as many Calories (9.3) of heat as 2 Gm. of a carbohydrate or protein in oxidation. There is available little information concerning the human requirement of fat. An average liberal diet for a man contains about 90 Gm. of fat every day.

**AS A RESERVE FUEL SUPPLY** The fat content of the body cells varies and it makes up as much as 90 per cent of some adipose tissues, where it serves as a concentrated reserve supply of chemical energy that is available when needed by the body. Ordinarily glycogen acts as a reserve supply of energy, but when it is used up, as in starvation, the body begins to burn its own fat as a fuel. Too much fat storage, however, interferes with the body's functioning.

**AS AN INSULATOR AGAINST LOSS OF HEAT** Because fat conducts heat very poorly, adipose tissue becomes a very good insulator for



Nourishment for such patients should consist largely of carbohydrates and proteins, and the amount of fat should be restricted

### Assimilation of Fats:

After absorption of the chyle by the intestinal mucosa the fatty acids and the glycerol recombine to form body fats which pour from the lymph vessels into the blood, and in the form of emulsions are carried to the cells where they are oxidized. All fats in excess of the amount required by the body for immediate energy are deposited as adipose tissue, which serves as a storehouse of available energy. The amount thus stored constitutes the major portion ingested. Body fat is permeated with a network of blood vessels which make it immediately available for use. An excessive amount of fat, of course, requires a greater number of blood vessels, and causes a strain upon the heart in forcing the blood through these veins.

A person who eats very much sugar, such as candy, is apt to become fat, for sugar (carbohydrate) in excess of that needed at the time is changed to body fat. In order that the fat may be oxidized in the body it is necessary to have blood sugar present. Blood sugar is normally present in sufficient quantities, but is not available when the pancreas fails to secrete sufficient insulin, which is necessary for both the storage and oxidation of glucose. Without insulin there is an inability to "burn" glucose, giving rise to a high sugar content which soon reaches the threshold point, then sugar begins to filter through the kidneys into the urine. This condition is called diabetes, it varies with the individual. Diets based on carbohydrate tolerance are used extensively in this disease. The available carbohydrate comes from 100 per cent of the carbohydrate, 58 per cent of the protein, and 10 per cent of the fat eaten, and is so figured in making a diabetic diet. It should be understood that a diabetic may eat any kind of food provided his sugar tolerance is considered. Every diabetic does not need insulin, since the need for insulin depends on the sugar tolerance.

In diabetes, wherein there is a faulty metabolism of sugar, the fat in the blood is often incompletely oxidized and certain fatty acids are formed which produce the acid condition known as *ketosis*. Acidosis results then, when the alkaline reserve of the blood and body is used up at a faster rate than it can be formed in taking care of the acids produced. Oxidation of these acids produces acetone, which is frequently found in the urine of diabetic patients, and



sometimes as a sweet odor on their breath. Acetone and the fatty acids, butyric acid, beta hydroxybutyric, and acetoacetic acids, are often referred to as "acetone bodies." Since the ingested sugars are not oxidized, the diabetic is not supplied with sufficient energy, but this condition may be remedied by the subcutaneous injection of insulin.\* Ketosis is often produced in normal individuals by feeding a diet high in fat and low in carbohydrate and protein. In epilepsy, many patients are improved by an acid condition and such a diet rich in fat has been employed extensively in the treatment of this disease.

Fats will be discussed further in the chapter on Metabolism.

### SELF-TESTING QUESTIONS

- 31 Name five important physiological functions of fats in the body.
- 32 Why do fats yield correspondingly larger quantities of energy than carbohydrates?
- 33 Explain the chief chemical changes taking place in the passage of ingested fat to body fat.
- 34 What emulsifies ingested fats?
- 35 What causes jaundice?
- 36 What conditions are necessary for oxidation of fat?
- 37 What are the functions of insulin?
- 38 What is acidosis and how is it caused?
- 39 How is a diabetic diet figured?

### V. OTHER LIPIDS

#### Some Complex and Derived Lipids\*

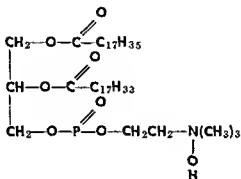
Waxes, like the animal and vegetable fats and oils which have just been considered, are classed as simple lipids. In chemical structure the waxes are esters which are derived from high molecular weight fatty acids and high molecular weight monohydric alcohols. These compounds come from both animal and vegetable sources and representative ones are beeswax, lanolin, spermaceti, and carnauba wax. Beeswax is to a large degree myricyl palmitate and ester, formula  $C_{15}H_{31}COOC_{31}H_{63}$ .

The compound lipids include *phospholipids* (phosphatides) and *glycolipids*. Substances of this nature, when hydrolyzed, give some product or products along with alcohols and fatty acids. Thus the glycolipids upon hydrolysis give a carbohydrate, usually galactose, as one of the decomposition products. Glycolipid structures exist

\* Since insulin is a protein and is capable of digestion, it must be injected hypodermically into the blood stream.

in brain tissue and for this reason have acquired the name cerebrosides

The *lecithins* are important phospholipids. Upon complete hydrolysis these complex esters yield glycerol, fatty acids, phosphoric acid, and a nitrogen base called *choline*. The latter substance has physiological significance since it prevents the accumulation of fat in the liver, and has the ability to lower blood pressure. Choline is also classed as a vitamin. The structure of a typical lecithin follows



The lecithin pictured here if subjected to a complete hydrolytic breakdown would yield glycerol, stearic acid, oleic acid, phosphoric acid, and choline,  $\text{HO}-\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_3)_3$ . In the body the



lecithins play a part in the transportation of fat and in fat metabolism, they may also serve as a source of phosphoric acid. In food industries the lecithins are widely used as emulsifying agents.

Closely related to the lecithins are the *cephalins*. In place of the choline, which is a part of the structure of a lecithin, the cephalins have other nitrogen bases, frequently ethanalamine,  $\text{HO}-\text{CH}_2\text{CH}_2-\text{NH}_2$ .

Associated with body fat as primary cell constituents are esters derived from fatty acids and complex cyclic alcohols called *sterols*. Such structures are classified as derived lipids, they have wide occurrence in both the plant and animal kingdoms. Two sterols of considerable importance are *cholesterol* and *ergosterol*. Cholesterol is present in the blood in a concentration which ranges from 140 to 200 mg per 100 ml of blood serum. Like the phosphatide,

lecithin, it is apparent that cholesterol also plays a part in regulating fat metabolism. With advancing age, cholesterol can be a contributing factor, if not the cause of arteriosclerosis. Certain hormones, and also vitamin D, are structurally closely related to cholesterol.

### SELF-TESTING QUESTIONS

- 40 What are phosphatides?
- 41 How do phosphatides resemble ordinary fat in physical and chemical properties?
- 42 In what ways are phosphatides important?
- 43 What interest is attached to cholesterol and ergosterol?

### SUGGESTED ACTIVITIES

#### I. THOUGHT PROVOKING QUESTIONS

- 1 Why is a fat referred to as a triglyceride?
- 2 How are fats and soaps related to fatty acids?
- 3 What is meant when it is stated that body fat is always in a liquid condition at body temperature?
- 4 Why would hydrogenation be of great economic and commercial importance during war times?
- 5 What chemical reaction would take place if salad dishes containing vinegar or acid foods were put in soapsuds?
- 6 Why is there a greater variation in the specific gravity of liquid fats than in solid fats?
- 7 Starting with fat, write the equations to show how nitroglycerine may be made.
- 8 Why should goods washed in cheap laundry soaps be thoroughly rinsed?
- 9 Upon standing exposed to the air, butter becomes rancid. What chemical reaction has taken place?
- 10 What is the difference in composition between natural fats and phosphatides? Between natural fats and sterols?
- 11 Why is it that onions cooked in fat have a different flavor than when cooked in water?
- 12 Which is more desirable for pastry making: a saturated or partially unsaturated fat? Why?
- 13 What are the precautions and reasons you would give in preserving butter?
- 14 In what way would a knowledge of the pH value of a fat be of some value?
- 15 Linseed oil contains the glyceryl ester of linolenic acid, the formula for which is  $C_{17}H_{33}COOH$ .
  - (a) What is the general series formula which includes this acid?
  - (b) How many double bonds are present? (c) Why does linseed oil dry more quickly than many other unsaturated fats?

**II VOCABULARY TESTING OF NEW TERMS**

glycolipids	choline	soap
phospholipids	cephalins	lipid
lecithins	fat	phosphatides
sterols	saponification	ketosis

**III TOPICS FOR ORAL AND WRITTEN REPORTS**

- 1 The History of Soap Making
- 2 Varieties of Soap
- 3 Theories Concerning the Cleansing Action of Soap
- 4 Germicidal Value of Pure Soap
- 5 *Edible Fats and Oils*
- 6 Relationship between Fat in the Diet and Cholesterol

**LABORATORY CHEMISTRY**

Laboratory exercises for this chapter will be found on page 725

## PROTEINS

## CHAPTER OUTLINE

- |  |  |
|--|--|
| <p><b>I OCCURRENCE, FUNCTIONS, FORMATION AND COMPOSITION</b></p> <p>(a) Occurrence and functions of proteins</p> <p>(b) Formation of proteins</p> <p>(c) Composition of proteins</p> <p><b>II, AMINES</b></p> <p>(a) Physical properties</p> <p>(b) Chemical properties</p> <p>(c) Quaternary ammonium compounds</p> <p><b>III AMINO ACIDS, THE STRUCTURAL UNITS OF PROTEINS</b></p> <p>(a) Chemical properties</p> <p>    1 Amphoteric action</p> <p>    2 Reaction with oxygen</p> | <p><b>IV PROPERTIES OF PROTEINS</b></p> <p>(a) Physical properties</p> <p>    1 Foam</p> <p>    2 Solubility</p> <p>    3 Colloids</p> <p>(b) Chemical properties</p> <p>    1 Heat</p> <p>    2 Precipitation</p> <p>    3 Hydrolysis</p> <p>    4 Color tests</p> <p>    5 Protein swelling and coagulation</p> <p>    6 Nitrogenous fibers</p> <p><b>V CLASSIFICATION OF PROTEINS</b></p> <p>(a) Simple proteins</p> <p>(b) Conjugated proteins</p> <p>(c) Derived proteins</p> <p><b>VI ASSIMILATION OF PROTEINS</b></p> <p><b>VII RECENT PROTEIN RESEARCH</b></p> |
|--|--|

## I. OCCURRENCE, FUNCTIONS, FORMATION, AND COMPOSITION

### Occurrence and Functions of Proteins:

Proteins exist in all living matter. They form the most important and most characteristic constituents of all living cells, and are present in all fluids of the body, except urine and bile. Carbohydrates and lipids, the chief reserve sources of energy for body activity, are also important constituents of the protoplasm of the body cells, but are secondary to the proteins, which are the chief components of the active tissues. Muscle tissues, for instance, are made up almost entirely of proteins and contain only small amounts of fats and carbohydrates. The word protein is derived from the Greek word meaning "to take first place." The proteins make up an extremely important group of organic compounds.

Since protein substances are *essential constituents of all living cells*, in that they provide building and repair materials, it is very evident that both animal and vegetable life are impossible without

them. Such organisms, however, may exist without food proteins for a varying time, but this period is one of existence rather than one of normal life. A lack of protein lowers the body's resistance to disease because without it, the normal amount of disease-fighting antibodies is not produced in the blood.



Fig. 1—Animal and Vegetable Proteins. How do animals and vegetables compare as sources of dietary protein? Courtesy National Dairy Council.

Proteins exist in both plants and animals, however, plants as a group contain very little protein, exceptions being the legumes, nuts, and seeds. Man derives a part of his proteins from such vegetables as beans, peas, nuts, and the seeds of grains (cereals),

but the larger part comes from such animal sources as meat, eggs, and milk products. Animal sources yield very high protein values. Although the same kind of carbohydrates and fats are found in both plants and animals, the proteins are not always of the same composition, and we must use a varied diet to get the different kinds of proteins necessary for the muscles, skin, hair, nails, blood, and tissues. Gelatin, though cheap, is a poor source of protein because it lacks two important amino acids (tyrosine and tryptophane), and as a sole source of supply would be quite inadequate. Skim milk powder however, is an excellent as well as a cheap source of protein.

The table below lists some common foods that are valuable sources of proteins.\* In particular, notice the percentage of protein in peanuts, cheese, and beans.

### Formation of Proteins:

The cells of only a few of the plants have the power of taking free nitrogen from the air. The so called leguminous plants, which include clover and alfalfa, build their own proteins (a) from the inorganic substances, such as sulfates, phosphates, nitrates, ammonium compounds and water absorbed by the roots; (b) from the carbon dioxide taken from the air by the leaves; and (c) from the nitrogen of the air that is transformed by the nitrifying bacteria of the roots into inorganic nitrogen compounds.

\* *Chemistry of Food and Nutrition*, Sherman, Macmillan Co

<i>Vegetable</i>	<i>Protein Percentage (Approximate)</i>	<i>Animal</i>	<i>Protein Percentage (Approximate)</i>
Beans (dried)	22.5	Cheese	25.0
Corn meal	9.2	Gelatin	17.9
Nuts		Eggs	13.0
Brazil	17.0	Meat	16.0
Peanuts	25.2	Milk	3.3
Walnuts (California)	12.4		
Oatmeal	16.1	NOTE: Milk is an economical and readily available source of protein, and in addition contains other growth favoring substances.	
Peas (dried)	24.6		
Wheat flour	11.4		

Animals also form the protein constituents of their own tissues, but cannot build proteins from simple inorganic substances, such as from the nitrogen of the air, or the nitrates and nitrites. Animals must depend for their nitrogen upon the proteins of the food they eat, and because the food of animals is obtained directly from plants, or from animals that live upon plants, the plant is the real "protein producer" of nature.

"Since animals must have proteins for the construction and repair of their own tissues, and since, broadly speaking, they cannot make their own proteins except from the cleavage or decomposition products of other proteins, it follows that proteins are necessary ingredients of the foods of all animals. It must not be overlooked that in addition to their function as a tissue builder, the proteins are upon oxidation a source of energy, equivalent, in amount, to that produced by an equal weight of a carbohydrate."\*

### Composition of Proteins:

The proteins differ in composition from the carbohydrates and fats chiefly in that they contain the element *nitrogen*. In addition to carbon, hydrogen, oxygen, and nitrogen proteins generally contain sulfur, less frequently phosphorus and a few other elements. Since the end products of oxidation of food proteins are acidic and decidedly so if the proteins contain sulfur or phosphorus, it should be remembered that in case of acidosis the more acid proteins should be eliminated from the diet. It is the presence of nitrogen which causes proteins to be so important, and makes them an indispensable part of the diet of every plant and animal.

The elements that make up proteins vary somewhat in the composition of the protein molecule. The following table shows the variations in which these elements occur.

Elements	Extremes of Percentage
Carbon	50.0 to 55.0
Hydrogen	6.0 to 7.3
Oxygen	19.0 to 24.0
Nitrogen	15.0 to 19.0
Sulfur	0.3 to 2.5 (when present)

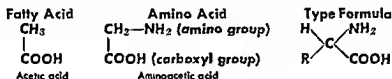
With a few exceptions the molecular weights and complete formulas of proteins are still uncertain quantities. The simplest

\* *Chemistry of Food and Nutrition* Sherman Macmillan Co.



formula that may be calculated from analysis shows that the molecules of proteins are large and very complex.

Recent experiment has shown that what were formerly thought to be protein molecules with molecular weights around 15,000 are, in reality, only fractions of their estimated molecular weights, and that molecular weights actually range between 43,800 (egg albumin), and 6,630,000 (hemocyanin). Notwithstanding their complexity, an examination of various protein molecules shows that they are composed of fatty acids into the molecule of which has been introduced the *amino group* ( $\text{NH}_2$ ), to form a class of substances called *amino acids*.



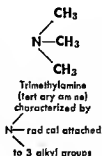
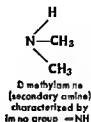
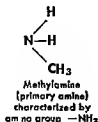
### SELF-TESTING QUESTIONS

1. What is the chief function of the proteins?
2. What are the vegetable sources of proteins?
3. Why must a varied assortment of proteins be included in our diet?
4. Why is milk considered as a good source of protein?
5. What are the protein producers of nature?
6. How do the proteins differ in composition from the carbohydrates and fats?
7. Chemically, how are the proteins formed?
8. Define a protein from its chemical formation
9. In what function are carbohydrates and proteins analogous?

## II. AMINES

Before proceeding with the study of the proteins it seems advisable to learn something about the nature of the amino group,  $\text{—NH}_2$ , which characterizes the amino compounds, and which also is a characteristic group in all proteins.

The simplest way of studying the aliphatic amines is (1) to consider them as *substituted "ammonias"* wherein one or more alkyl radicals have been substituted for hydrogen in the ammonia molecule, the classification depending upon the number of H atoms replaced,



and (2) to consider their properties as being very similar to those of ammonia

### Physical Properties:

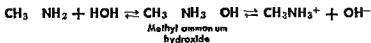
From a physical standpoint, the simplest amines resemble ammonia by being gases that have a somewhat similar odor and are soluble in water. As the complexity of the molecules increases, the amines become liquids or solids with a corresponding decrease in their solubility and in their flammability.

### Chemical Properties:

**1 AMINES REACT WITH WATER TO FORM IONIZABLE BASES**  
Chemically, the amines closely resemble ammonia, except for their combustibility. Both ammonia and amines form *weak bases* in water. Strictly speaking, ammonia does not become a base until it has united with water to form ammonium hydroxide



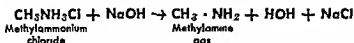
In the same way an amine does not become a base until it has united with water



**2 AMINES REACT WITH ACIDS TO FORM IONIZABLE SALTS**  
An amino compound acts as a base, just as ammonia does, in that the amino compound ionizes and reacts with acids to form salts. A comparison between the action of ammonia with an acid and an amine with an acid to form salts, in which the valence of nitrogen is five, is shown in the following equations



3 AMINE SALTS ARE DECOMPOSED BY STRONG BASES Furthermore, amines resemble ammonia in that the amine is liberated from its salts when heated with stronger bases



From this discussion it should be particularly remembered that the  $\text{NH}_2$  group gives basic properties to a compound

The aromatic amines, of which the simplest one is aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ , closely resemble the aliphatic amines in classification and properties. A number of compounds which have value in medicine are derived from aniline and other aromatic amines

#### SOME DERIVATIVES OF AROMATIC AMINES USED IN MEDICINE

Amine	Uses
Acetanilide	Analgesic (relieves pain when given by mouth) Antipyretic (reduces fever temperatures)
Arsphenamine (salvarsan)	Specific for treatment of syphilis in all stages particularly in primary stage
Phenacetin	Antipyretic      Commercial headache and neuralgia remedies
Sulfa Drugs e.g., Sulfanilamide Sulfadiazine Sulfathiazole	Primarily in infections due to hemolytic streptococci but also effective in pneumonia and other infections. Active against nearly all true bacteria

Complex amines are found to a considerable extent in nature under the name of alkaloids, compounds which have already been discussed (p 192). Amines are sometimes formed in the body as the result of the action of putrefying bacteria upon the proteins. This gives rise to a class of poisonous substances called "ptomaines"

NOTE: An amide is an organic acid in which the OH of the  $\text{COOH}$  group has been replaced by an  $\text{NH}_2$  group or it may be considered as  $\text{NH}_3$  with one H replaced by an acyl group,  $\text{R}-\text{C}=\text{O}$

## Quaternary Ammonium Compounds

In recent years a number of synthetic quaternary ammonium compounds (so called because the nitrogen in the molecule is joined to four carbon atoms) have been finding extensive use. The cationic "quats" are very effective germicidal and bacteriostatic agents, but in this property they are inactivated by the presence of anionic detergents, soap, and protein containing substances making them ineffective in the presence of blood or pus. Many hospitals use "quats" in various concentrations for a variety of disinfectant and antiseptic purposes, both on patients' skin and mucous membranes, and on many types of equipment. The quaternary ammonium salts are also effective cationic detergents.

## III. AMINO ACIDS: THE STRUCTURAL UNITS OF PROTEINS

With some understanding of the nature of the amino group we are now ready to study the properties of the amino acids, compounds which are called the "building stones of the proteins." Some twenty three different amino acids connected with body chemistry are definitely known, of which number a certain few are absolutely necessary in our daily diet if life is to continue (p. 611). In all, over thirty different amino acids have been obtained as derivatives of the proteins. Since all amino acids are synthesized by the plant cell through a photosynthetic process it is understandable how dependent we are upon plant life for our vital proteins.

Before proceeding with the study of amino acids it is well to keep in mind that amino acids are organic acids with an amino group ( $\text{NH}_2$ ) substituted for a hydrogen atom in the alpha\* ( $\alpha$ ) position, i. e., on the carbon atom next to the carboxyl group.

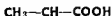
The following list shows  $\alpha$  aminoacetic acid, the simplest of all amino acids,  $\alpha$  aminopropionic acid, the next simpler acid, from which all other amino acids are structurally derived and the several different types of amino acids.

### AMINO ACIDS

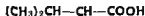
#### I One amino group for each carboxyl group



Glycine  
(aminoacetic acid)

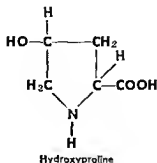
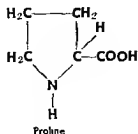
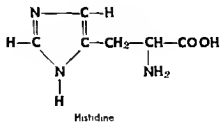
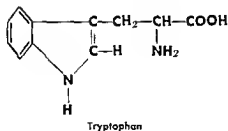
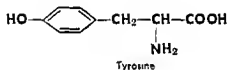
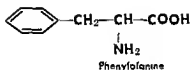
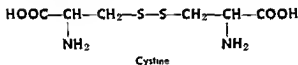
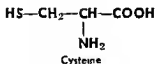
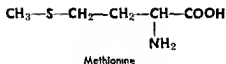
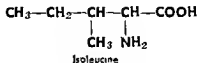
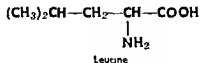
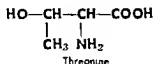
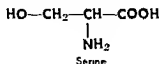


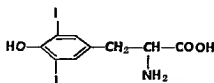
Alanine  
( $\alpha$  aminopropionic acid)



Valine

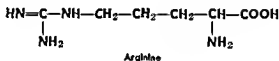
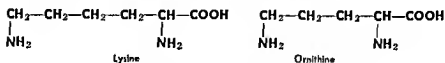
\* The first carbon next to the acid ( $\text{COOH}$ ) group is called the alpha ( $\alpha$ ) carbon atom the second carbon atom is the beta ( $\beta$ ) the third is the gamma ( $\gamma$ ), and so on.



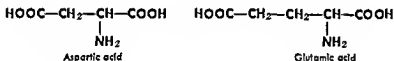


Iodogorgoric acid

## II Two amino groups for each carboxyl group

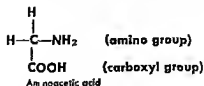


## III Two carboxyl groups for each amino group



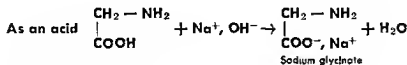
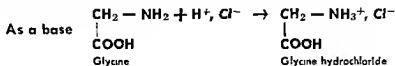
## Chemical Properties of Amino Acids

1 **AMPHOTERIC ACTION** It may be noticed in the following amino acid molecule that there is an *acid* (COOH) and a *basic* (NH<sub>2</sub>) group

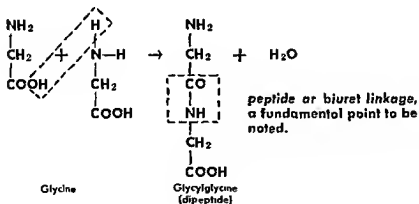


These two groups make it possible for the compound to act as a base or an acid. Such compounds are said to be *amphoteric*.

The following reactions of aminoacetic acid, commonly called glycine, with an acid and with a base illustrate the amphoteric properties of an amino acid.

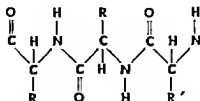


This dualistic nature of the amino acids accounts for their ability to combine with each other, and in that way build up the complex protein molecule. The linkage of amino acid radicals through the acid carboxyl group (COOH) of one to the basic amino group (NH<sub>2</sub>) of another is illustrated thus:

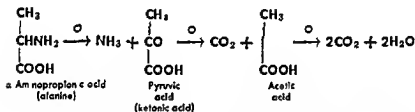


In the dipeptide, the linkage  $\begin{array}{c} \text{O} \quad \text{H} \\ || \quad | \\ -\text{C}-\text{N}- \end{array}$  is called the *peptide* or the *biuret linkage*.

Continued combination between more amino acids by condensation eventually builds polypeptides, peptones, proteoses, and finally proteins. From the above it is quite evident that *proteins are combinations of amino acids*. The following notation expresses in a general way the nature of the polypeptide chain:



**2 REACTION WITH OXYGEN** Of particular interest and great importance to the nurse is the understanding of what reaction takes place in the human body when amino acids, in excess of those needed for tissue building, undergo oxidation to produce heat and energy. In this oxidation change the amino group is removed to form ammonia and a ketone acid. Using alpha amino propionic acid commonly called *alanine* as an example the following equation shows what probably takes place in the stepwise oxidation.



Further discussion of the place of amino acids in the tissues will be presented in the chapter on Metabolism (p. 495).

### SELF-TESTING QUESTIONS

- 10 Explain the statement: amines are substituted ammonias.
- 11 State three chemical properties of amines that are similar to the properties of ammonias.
- 12 Name two important aromatic amines and their uses.
- 13 Name a class of naturally occurring drugs which are amines.
- 14 To what class of compounds do ptomaines belong?
- 15 Why is a protein amphoteric?
- 16 What is the peptide or biuret linkage?
- 17 How are proteins formed?
- 18 Define a protein.



#### IV. PROPERTIES OF PROTEINS

The properties of the proteins are not very clearly defined, even though they do have many common characteristics. What differences do arise in the nature of the many different and complex proteins are for the most part due to the number, the kind, and the arrangement of the various amino acids within the protein molecule. Thus albumin, pepsin—an enzyme—and insulin—a hormone—are proteins of varying natures. However, with the understanding that proteins are complex molecules of large molecular weight, are combinations of amino acids, and can act as acids or bases, the study of their behavior is less difficult.

##### Physical Properties:

The *physical properties* of the proteins are due largely to their behavior as colloidal substances. Their most characteristic physical properties follow.

**FOAM** The proteins are mostly colorless and amorphous compounds, only a few being colored (hemoglobin) and crystalline. For the most part, they are typical colloidal substances which foam readily when in solution. Milk or blood, for example, foams when agitated as a result of the colloidal material present.

**SOLUBILITY** There is quite a variation in the solubility of the proteins. Some, like the *albumins*, are soluble in plain water and in salt solutions, others, like the *globulins*, are soluble only in salt water, while still others are soluble only in an acid or alkali medium. All are insoluble in the common solvents for fats, such as ether.

**COLLOIDS** Most of the soluble proteins on account of their high molecular weight form colloidal dispersions which do not diffuse through an animal membrane, a very important factor in regulating cell activity. If it were not for this nondiffusible property, all soluble proteins would be excreted through the kidneys and not be retained in the blood stream. It is only when the kidneys are diseased that the cells are permeable and albumin is found in the urine.

Elsewhere (p. 111) it has been stated that proteins are positive in a medium more acid than the isoelectric point and negative in a medium which is less acid than the isoelectric point. Proteins are colloids and adsorb water (p. 113), and acids or bases increase the

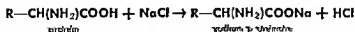
adsorption of water and make protein foods more tender  
Most proteins have a negative charge in a neutral solution

### Chemical Properties

**1 PROTEINS ARE DECOMPOSED BY HEAT** The chemical behavior of the proteins is that of the amino acids of which they are composed. When heated, they gradually decompose, giving off a strong odor like burnt wool or hair, and when in a colloidal dispersion they may be precipitated by a variety of agents, all depending upon the kind of proteins present.

**2 PROTEINS ARE PRECIPITATED By Heat** Under the influence of heat the molecules of a dispersed protein tend to run together to form an insoluble protein. This form of precipitation or coagulation is called *denaturation*. It differs from ordinary precipitation in that the *change is permanent* and the albumin now a denatured protein, cannot be restored to its former state though it can be dissolved by acids, bases, urea and other reagents. The change and appearance of the white of an egg after cooking are a good example of coagulation, a condition which increases the digestibility of egg albumin, hemoglobin, and many other proteins. Since living cells contain proteins, heat coagulates and kills them. The spores of certain bacteria, however, are very resistant to heat. This is because they contain very little water and are coagulated only at extreme degrees of heat. This resistance of spores and dried proteins to coagulation accounts for the superiority of moist heat (steam) over dry heat in sterilization. From the preceding statements it is evident that heat may sometimes be used as a simple test for a soluble protein, such as albumin in pathological urine.

**By Salts of Heavy Metals** ( $\text{HgCl}_2$ ,  $\text{AgNO}_3$ ,  $\text{CuSO}_4$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) Since proteins can act in part as acids because of the  $-\text{COOH}$  group it is evident that proteins may react with salts to form other acids and salts, e. g.,



The sodium salts of dispersed proteins can be expected to be soluble. Some metallic salts though, may form insoluble proteinates. For example, salt solutions of heavy metals have long been used for their antiseptic and germicidal properties since they coagulate proteins. Bichloride of mercury is one of the very im

portant disinfectants, but even so it may not be used for this purpose when the parts to be sterilized contain a great deal of protein (vomit, stools, etc.), since in the coagulation the mercuric chloride combines and forms with the proteins an enveloping capsule that prevents further penetration of the antiseptic. Thus in the case of poisoning from bichloride of mercury, it is easily understood why the white of egg or milk is introduced into the stomach of the patient. Even though the absorption and distribution of the poison are retarded, there is a tendency for the coagulated protein to redissolve in the course of digestion and to be absorbed to attack the tissues, especially the kidneys. For that reason, immediate action should be taken to remove the contents of the stomach.

Silver compounds are widely used in medicine to produce caustic, astringent, and antiseptic effects, actions which are largely due to free silver ions. Such a compound is silver nitrate, which coagulates cell constituents and secretions by entering into chemical combination with the proteins present. This action has a tendency to stop any further caustic effect, and the antiseptic action that follows is due to the slow freeing of silver ions from the silver protein compounds that had been formed.

The value of lead acetate as a skin antiseptic, and copper sulfate as a spray (Bordeaux mixture), is also based upon this coagulating effect.

*By Alcohol* Alcohol is a very common antiseptic, in that it coagulates bacteria (proteins), but if the alcohol is 95 per cent there is very little germicidal action, because like the bichloride of mercury, the formation of a protective envelope keeps the alcohol from passing through the protein, and at the same time withdraws water from the bacteria. The addition of water revives them. In hospitals, a 70 per cent alcohol solution is generally used on the wards for antiseptic purposes and as an alcoholic rub because at this concentration bacteria are killed rapidly. The water probably keeps the alcohol in contact with the bacteria a longer time and prevents too rapid evaporation.

*By Acids* Since the proteins also have a basic group,  $-NH_2$ , in their molecules they may react with acids to form salts, some of which are insoluble.

The organic acids, picric, tannic, and phosphotungstic, are principally used for the purpose of precipitating proteins, and are often called alkaloidal reagents. Advantage is taken of this effect in using picric acid as a coagulating test for albumin in the urine (Eshach's

test) In the leather industry, tannic acid extracted from the bark of certain trees (oak hemlock) renders protein hard and free from bacterial action Tannic acid (and sometimes picric acid) is also used in the treatment of burns to combat shock, toxemia and sepsis (poisoning of system) As an astringent it contracts the tissues to lessen the secretion of the precious body fluids, to prevent the absorption of toxic protein disintegration products resulting from the injured tissues, and to relieve pain by protecting exposed nerve endings with a restraining eschar over the burned area Frequently this treatment is followed with a dilute solution of silver nitrate Spraying sulfadiazine directly on burns is still hailed as a very effective treatment

The bitterness or puckering sensation of strong tea and of underripe fruits is due to the effects of tannic acid on the proteins of the mucous membranes

*The inorganic acids* also precipitate proteins This action is put to good advantage in using nitric acid to make a test for albumin in the urine, the acid precipitating a ring of protein at the junction of the urine and the acid (Heller's ring test) With an excess of the acids, the precipitated proteins act as a base and redissolve Also, in the presence of an excess of strong alkali the precipitated proteins act as an acid and dissolve This explains the action of both acids and bases upon wools (p 159) It is also on account of this dualistic nature of the proteins that we are able to explain how the protein assists in regulating the acid base balance of the blood (p 186)

*Precipitation Explained* From the foregoing it is evident that the proteins may be precipitated unaltered or as insoluble salts Also, the addition of some salts like sodium chloride, ammonium sulfate, and magnesium sulfate will remove water from the colloidal protein particles and cause them to "salt out" or precipitate It is in a similar way that alcohol precipitates proteins On the other hand, the insoluble state may be due to a chemical reaction

Proteins are amphoteric substances and therefore they may behave as either acids or bases depending upon the  $pH$  of the environment In a medium more acid than its isoelectric point a dispersed protein exists primarily as positive ions Consequently it can react with the anions of certain acids to form insoluble salts The addition of tannic acid to produce an insoluble protein tannate illustrates this


When a protein is dispersed in a medium which is less acid than



The proteins differ mainly in the number and kind of amino acids produced by hydrolysis, some proteins not even producing the amino acids which are necessary to maintain growth or even to sustain life (p. 611). From this statement it is evident that the biological value of proteins is mostly determined by the amino acids formed on hydrolysis, and that any deficiency in the number or variety limits their value. As previously stated, some twenty-three different amino acids are known in connection with body functions.

In connection with this it should be remembered that the digestion of all foods, as carbohydrates, fats, and proteins, is a series of hydrolyses which break the complex molecules into simpler ones.

4. PROTEINS GIVE COLOR TESTS: Tests for proteins are not only dependent upon precipitation or coagulation but also upon color reactions with certain reagents. The best known color tests are *Millon's* and the *biuret test*. Heating a protein with Millon's reagent (mercury dissolved in nitric acid) produces a brick red color

Test Name	Reagent Composition	Color	Cause of Color
Biuret	Strong alkali and a few drops of dilute $\text{CuSO}_4$	Violet shade	2 biuret or peptide linkages $\begin{array}{c} \text{O} \quad \text{H} \\    \quad   \\ -\text{C}-\text{N}- \end{array}$
Millon's	Mercury metal dissolved in conc. nitric acid, then diluted	Reddish	Hydroxylphenyl group $-\text{C}_6\text{H}_4(\text{OH})$ (tyrosine group)
Xanthoproteic	$\text{HNO}_3$	Yellow, deepening to orange when acid is neutralized with alkali	Benzene ring, as Tyrosine Tryptophan Phenylalanine
Hopkins-Cole	Glyoxalic acid $\text{CHO}-\text{COOH}$	Violet	Indole group of Tryptophan 

or precipitate, while with the biuret reagent (a few drops of dilute  $\text{CuSO}_4$  in concentrated  $\text{NaOH}$ ) it produces a violet to pink color (dipeptides excepted). A very familiar protein reaction is the yellow color produced by nitric acid on the skin. Upon the addition of an alkali the color changes to an orange, giving what is known as the xanthoproteic or "yellow protein" test. Since there is a variance in the kind and number of groups in different proteins, there will be various color tests. As a consequence too much reliance should not be placed upon a single test to indicate the nature of a protein. The most important color tests for proteins are shown in the table on page 394.

### **Protein Swelling and Coagulation.**

As has been stated (review, p. 111) proteins are neutral at the isoelectric point but become positive in a more acid solution, and negative in a more alkaline solution. When acid to the isoelectric point, the colloidal proteins in the body have a great affinity for water. Thus an accumulation of lactic acid as the result of violent exercise or delayed metabolism produced by anesthetics or toxins can result in swelling. To repress this swelling (edema) certain salts (alkali tartrates, acetates, phosphates), or fruit acids have been recommended.

According to some authorities anesthesia is due to a coagulation of some of the proteins of the brain and sensory nerves. Habit-forming drugs, such as morphine, coagulate nerve proteins and act as they do because they are not eliminated very rapidly, whereas the true anesthetics (ether, nitrous oxide, chloroform) are eliminated from the body in a very short time.

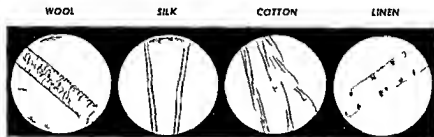
A brief discussion of allergic reactions caused by proteins is presented on page 436.

### **Nitrogenous Fibers:**

Animal fibers such as hair, wool, and silk belong to a class of proteins called keratins, compounds which are characterized by their great insolubility in neutral solvents, but being proteins, they are amphoteric and therefore are capable of reacting as bases or acids. For instance, wool and silk readily dissolve in 10 per cent sodium hydroxide solution, and turn yellow in warm nitric acid (xanthoproteic reaction). Cold, concentrated hydrochloric acid,

however, has little effect on wool, and dissolves silk but very slowly. When ignited, animal fibers burn only so long as they are held in the flame, give off an odor like burning hair, and form a small tarry knob at the end of the fibers. Wool in particular is very sensitive to heat, the fiber becoming very brittle at  $100^{\circ}\text{C}$ .

Under the compound microscope all fibers, whether animal or vegetable in nature, show definite characteristics.



Courtesy, Microanalytic Division, Food and Drug Administration

Cells overlap  
like scales

Smooth, solid  
round

Flattened, twisted,  
resembles deflated  
tube

Irregular, jointed  
strands. Resembles  
bamboo stems.

Fig. 2

Two important synthetic nitrogenous fibers have been produced. These are *Lanital*, a woolen substitute made from casein, and *nylon*, a silk substitute made basically from coal, air, and water. Nylon has proved to be a very successful synthetic, and is widely used for hosiery and other wearing apparel, bristles for brushes, surgical sutures, machine bearings, and a host of other things. Undoubtedly it has brought about a curtailment of the natural silk industry.

### SELF-TESTING QUESTIONS

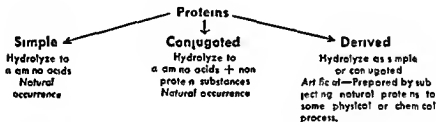
- 19 State the physical properties of proteins.
- 20 How do the proteins differ in their solubility?
- 21 What is a simple test for a soluble protein?
- 22 What metallic salts form insoluble proteinates?
- 23 What are the functions of a 70 per cent alcoholic solution on the skin?
- 24 What is Heller's ring test?
- 25 What medicinal advantage is taken of the coagulation action of picric and tannic acids on proteins?



- 26 Why are proteins soluble in both acids and alkalis?
- 27 How may proteins be separated from solution unaltered?
- 28 To what principle is this latter separation due?
- 29 What intermediate products are formed upon hydrolysis of proteins?
- 30 What are all tests for proteins based upon?
- 31 State two color tests for proteins
- 32 How do you account for swelling in proteins?
- 33 What effect do anesthetics and alkaloids have upon proteins of the brain and sensory nerves?

## V. CLASSIFICATION OF PROTEINS

The number of different proteins is almost unlimited. Certain proteins have similar characteristics, and accordingly they may be placed in three principal classes: the *simple*, the *conjugated* or compound, and the *derived* proteins.



### Simple Proteins:

The simple proteins are the native or *true* proteins which upon complete hydrolysis yield amino acids only.

The principal members of simple proteins are the albumins and the globulins. Both of these occur in blood serum, in the white of eggs, in meat, in the whey of milk, in the gluten and legumin of plants, in the myosin of muscle protein, and the fibrinogen of blood plasma. Their properties are very similar, differing chiefly in their solubility in water and in salt water. The albumins are very abundant in animal fluids (blood, etc.) while the globulins predominate in the tissues. Since both the albumins and globulins form colloidal dispersions in very dilute salt solution it is evident that the boiling of meat in a dilute salt solution, as in the preparation of soups or stews, results in the extraction of these nutritive proteins.

## CLASSIFICATION OF SIMPLE PROTEINS

Subdivision	Properties Solubility and Effect of Heat (Basis of Classification)					Examples and Remarks
	H <sub>2</sub> O	Salt Sol	Dil Acid or Alkali	Alcohol	Coag by Heat	
Albumins	+	+			+	Ovalbumin (egg white), serum albumin (blood), lactalbumin (milk), vegetable albumins Abundant in animal fluids
Globulins		+			+	Serum globulin, muscle globulin (myosin) veg etable globulins Predominate in the tis sues
Glutelins			+		+	Glutenin (wheat)
Prolamines				+ 70 to 80		Gliadin (wheat), zein (corn)
Albuminoids						Collagen (tendon) Kera tin (hair, hoof horn) Elastin (ligament) Principal part of skel etal structure and pro tecting tissue
Histones	+		+			Globin (blood) Basic proteins
Protamines	+					Salmina (salmon sperm) Simplest of natural proteins a polypeptide Basic properties no food value precipitates solu tions of other proteins

Myosin, a muscle protein, is a globulin, the coagulation of which, after death, produces what is called *rigor mortis*.

### Conjugated Proteins:

Conjugated, or compound, proteins are those which have a protein molecule united to some other molecule of a nonprotein substance. Upon *hydrolysis* they yield both amino acids and non-protein substances. The following table is a classification based upon the nature of the nonprotein constituent.

#### CLASSIFICATION OF CONJUGATED PROTEINS

<i>Subdivision</i>	<i>Compound Proteins (Basis of Classification)</i>	<i>Examples and Remarks</i>
Nucleoproteins	Protein + nucleic acid	Nucleoproteins in thymus, spleen, pancreas, glandular tissue Hydrolyze to purine bases
Glycoproteins	Protein + carbohydrate-group	Mucin (saliva, body secretions) Hydrolyze to yield a sugar which reduces Benedict's solution
Phosphoproteins	Protein + phosphate-group	Casein (milk), vitellin (egg yolk)
Hemoglobins	Protein + hematin (iron compound)	Hemoglobin (blood) Hydrolyzes to histone, globin and hematin
Lecithoproteins	Protein + lecithin	Fibrin, egg yolk

Blood contains the soluble simple protein fibrinogen (globulin), which upon exposure to air coagulates and is changed into an insoluble conjugated protein called *fibrin*. The most accepted theory (Howell's) to account for the formation of the blood clot is presented elsewhere (p 448).

### Derived Proteins:

The derived proteins, as the name implies, are an artificial group obtained from the simple and conjugated proteins by the action of

*acids, alkalis, heat, or enzymes. They are less complex than the simple or conjugated proteins and do not occur in nature. Upon hydrolysis the derived proteins again divide into two groups, the primary and the secondary derivatives; the primary are the result of a very slight hydrolysis, while those of a more extended hydrolysis represent the secondary derived proteins. The classification based upon their hydrolytic changes is shown in the following table.*

### CLASSIFICATION OF DERIVED PROTEINS

Subdivision		Derived by Hydrolysis (Basis of Classification)	Examples
Proteins		Insoluble proteins produced by water, enzymes, acids	Casein (curdled milk) Fibrin (coagulated blood)
Primary	Metaproteins	Insoluble proteins produced by further hydrolytic action of water, enzymes, and acids Soluble in weak acids and alkalis	Acid metaprotein Alkali metaprotein
	Coagulated Proteins	Insoluble proteins, the result of heat and of alcohol	Cooked egg albumin
Secondary	Proteoses	Soluble in $H_2O$ , precipitated by saturated $(NH_4)_2SO_4$ solution Slightly diffusible	Protoproteose Deuteroproteose
	Peptones	Soluble in $H_2O$ , not precipitated by saturated $(NH_4)_2SO_4$ More diffusible	Antipeptone Amphopeptone
	Peptides	Soluble in $H_2O$ , simplest combinations of two or more amino acids Very diffusible	Di-, tri-, tetra-, and pentapeptides

### VI. ASSIMILATION OF PROTEINS

The proteins, according to present view, are transformed partly in the intestinal contents and partly in the intestinal mucosa into amino acids, which either pass to the cells to build tissue, or to the liver where they form urea. Further discussion is presented in the chapter on Metabolism.

## VII. RECENT PROTEIN RESEARCH

The investigation of proteins is a field of very active biochemical research, and in concluding this chapter it is appropriate to give brief attention to some of the newer developments. Three areas of intensive study are to be noted: (1) analysis and synthesis of protein molecules, (2) the "gross" nature of proteins, and (3) the significance of the nucleoproteins.

(1) As we have learned, natural protein molecules are exceedingly complex with molecular weights so great that they can truly be called *macromolecules*. Yet all proteins, regardless of source or complexity, are the result of joining together numerous amino acids via peptide linkages. Some thirty different alpha amino acids have been found in the proteins. There are two general approaches to acquiring insight into the protein molecule, namely analysis and synthesis. It is to be noted that characterizing the structure of a given protein requires knowing not only which amino acids are present and how many residues of each, but also the sequence in which the various amino acid residues appear in the polypeptide chain.

Three protein type substances have at this time been studied to the point where their structures are believed to be known. These are insulin, a hormone, ribonuclease, an enzyme, and the tobacco mosaic virus. All of these are relatively simple proteins, and in fact they might better be characterized as enormous polypeptides. For example, ribonuclease contains 124 amino acid residues. In each case the elucidation of structure came about by analysis, *i.e.*, by hydrolysis of the natural substance into fragments which could be identified. Synthesis has also proved useful. Biochemists have succeeded recently in synthesizing a polypeptide made up of twenty three amino acids which shows the biological activity of ACTH (adrenocorticotrophic hormone). Hence it can be said that the portion of the ACTH structure in which the biological activity resides has been synthesized in the laboratory. In the body, ACTH is secreted by the pituitary gland.

(2) We turn now to a consideration of the over all or gross structures of the proteins. Much of the information of this nature has come to light by the use of the electron microscope and the x ray. The problem is more physical than chemical since it becomes a matter of determining how the long polypeptide chains are oriented in the structure of the protein. Proteins appear to have

two general shapes, globular or fibrous. In the silk protein fibroin, it is believed that the polypeptide chains have a zigzag form and lie side by side, with cross links to hold them together. The alpha keratin protein of hair is considered to have a helical, spiral like shape. In the globular proteins the chains of polypeptides are possibly twisted like a loose tangle of string, or folded in a pleated fashion.

(3) All living cells contain nucleoproteins. By classification these are conjugated proteins. When a nucleoprotein is partially hydrolyzed each molecule gives a protein molecule and a non protein molecule. The nonprotein portions are known as the nucleic acids. These in turn are very high molecular weight substances which are made up of sequences of residues of nitrogen bases (purines and pyrimidines), pentose sugar and phosphoric acid. Those having the sugar *ribose* as part of the structure are termed RNA (*ribonucleic acid*) while those containing the sugar *deoxyribose* are termed DNA (*deoxyribonucleic acid*). As many as 5000 of the nitrogen base pentose sugar phosphate sequences (mono nucleotide units) are present in DNA.

There is now evidence to support the belief that the nucleic acids enable the cells to store and transmit genetic information. DNA plays a significant role in chromosomes. Theories concerned with the ability of the nucleic acids to control the synthesis of molecules and to transmit hereditary traits point to the possibility of some exciting discoveries about the nature of life itself.

### SELF-TESTING QUESTIONS

34. Upon what basis are the proteins classified?
35. Discuss the occurrence and difference in solubility of two simple proteins.
36. What causes *rigor mortis*?
37. Account for the formation of the blood clot and then classify the proteins involved.
38. How are the derived proteins obtained?
39. What happens to the amino acids after leaving the intestine?
40. What is a macromolecule?
41. What are the two general physical shapes shown by proteins?
42. What is the relationship of nucleoproteins to nucleic acids?

### SUGGESTED ACTIVITIES

#### I. THOUGHT PROVOKING QUESTIONS

1. How are the amines classified?
2. Why is  $\text{HgCl}_2$  an excellent germicide?

- 3 How do you account for the fact that blood serum when diluted with water will become cloudy, but when diluted with physiological saline solution there will be no cloudiness, rather a clear solution?
- 4 When might not  $\text{HgCl}_2$  be effective as a disinfectant?
- 5 In making nutritive broth why should the meat be placed in cold salt water?
- 6 In preparing a meat by stewing why cover with hot, clear water?
- 7 In using beaten egg white to make cakes why do they not "fall" after baking?
- 8 Name several astringents used in nursing procedures and explain why they are so used
- 9 Name five important amino acids that cannot be synthesized by the body and state the function of each
- 10 How is thyroxin formed in the body and how does it function?
- 11 Why regulate the protein of a diabetic?
- 12 In cleaning milk bottles, dishes with egg on them, and fabrics stained with blood or mucous secretions, why should cold rather than hot water treatment be the first procedure in attempting to remove the clinging proteins?
- 13 How may the amino acids in body cells lymph and blood assist in maintaining a normal pH in these fluids?
- 14 In preparing a meat stock for soups why is salt added before the meat is cooked?
- 15 How successful have chemists been in synthesizing proteins?
- 16 The fact that wet hair can be stretched suggests what kind of physical structure for the protein of hair?

## II VOCABULARY TESTING OF NEW TERMS

protein	amino group	conjugated proteins
amphoteric	amines	derived proteins
peptide linkage	simple proteins	amino acid

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Chemical Changes during Cooking of Proteins
- 2 The Relationship of Amino Acids to Proteins
- 3 The Problem of Complete and Incomplete Proteins in the Diet

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 729

## REVIEW OF DEFINITIONS

## CHAPTERS XII THROUGH XVII

The following terms are important in the study of chemistry. A familiarity with them will help in building a scientific vocabulary that will be invaluable.

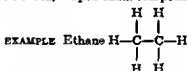
*acidosis* (as id o sis) A pathological condition in which acetone and certain acids are present in the body in abnormal amounts

*alcohol* Hydroxyl substitution product of a hydrocarbon

EXAMPLE  $\text{CH}_3\text{OH}$  methyl alcohol

*aldehyde* (al de hide) The first oxidation product of a primary alcohol. A hydrocarbon wherein a hydrogen has been replaced by the  $-\text{CHO}$  group

*aliphatic compounds* (al e-fat ik) Open chain compounds



*amines* (am ins) A group of organic compounds containing the amine ( $\text{NH}_2$ ) group. They are substituted ammonias

EXAMPLE  $\text{CH}_3\text{NH}_2$  methylamine

*amino acids* Compounds derived from the fatty acids by the exchange of a hydrogen atom of the hydrocarbon radical for an amino group

EXAMPLE  $\text{CH}_3(\text{NH}_2)\text{COOH}$ , aminoscetic acid

*amino group* (am in-o) The  $\text{NH}_2$  group which characterizes the amines

EXAMPLE  $\text{CH}_3\text{NH}_2$ , methylamine

*amphoteric compounds* (am fo-ter ik) Compounds that may act either as a base or an acid

EXAMPLE Protein

*aromatic compounds* Ring or cyclic compounds related to benzene  $\text{C}_6\text{H}_6$ . Many have fragrant odors

EXAMPLE Methyl salicylate (oil of wintergreen)

*biological chemistry* Study of chemistry of life

EXAMPLE Study of digestion



**carbohydrates** (kar ho-hi drates) A group of compounds including the sugars, starch, gums, and cellulose. They contain hydrogen and oxygen in the ratio of two to one, with but a few exceptions.

EXAMPLES  $C_6H_{12}O_6$ ,  $C_{12}H_{22}O_{11}$ ,  $(C_6H_{10}O_5)_n$

**carbonyl** (kar'bon il) A characteristic group in aldehydes and ketones

EXAMPLE  $=C=O$

**carboxyl** (kar box il) The characteristic group of an organic acid

EXAMPLE  $-COOH$

**conjugated proteins** Compounds which upon hydrolysis yield amino acids and a nonprotein substance

EXAMPLE Hemoglobin

**derived proteins** Compounds obtained from simple or conjugated proteins by the action of acids, alkalies, heat and enzymes

EXAMPLE Proteoses, peptones, peptides

**disaccharides** (di sak ar ids) Carbohydrates which will hydrolyze into two molecules of monosaccharide

EXAMPLE  $(C_6H_{10}O_5)_2 \cdot H_2O$  or  $C_{12}H_{22}O_{11}$

**es'ter** Compound formed by the displacement of the hydrogen of an acid by a hydrocarbon radical

EXAMPLE  $C_2H_5NO_2$ , ethyl nitrite

**ether** A hydrocarbon oxide

EXAMPLE  $(C_2H_5)_2O$ , ethyl ether

**fat** A glyceryl ester of a fatty acid

EXAMPLE  $C_2H_5(C_{18}H_{35}O_2)_3$  glyceryl stearate (stearin)

**fermenta'tion** The reaction of bacteria, yeasts, or molds on carbohydrates

EXAMPLE Alcoholic fermentation of glucose

**fractional distilla'tion** Separation of liquids based upon the difference in their boiling points

**glycosuria** (gli ko su're-a) A condition wherein an abnormal amount of sugar is found in the urine

**heterocyclic** (het-er-o-si'klik) Pertaining to ring compounds which contain other atoms in addition to carbon atoms, as part of the ring

EXAMPLE Furan 
$$\begin{array}{c} \text{CH}=\text{CH} \\ | \quad \diagup \quad \diagdown \\ \text{CH}=\text{CH} \quad \text{O} \end{array}$$

**homologous series** (ho-mol o gus) Compounds with similar chemical structure and properties, and arranged in order of their molecular complexity

EXAMPLE Methane ( $CH_4$ ), ethane ( $C_2H_6$ ), etc

*hydrocarbon* A compound composed of carbon and hydrogen

EXAMPLE  $\text{CH}_4$ , methane

*hydrogenation* A process of changing an unsaturated fat to a solid saturated fat by the addition of hydrogen in the presence of a catalyst (Ni)

EXAMPLE Olein to stearin

*hydrolysis* (hi dro l i s i s) Any chemical decomposition reaction involving water

EXAMPLE  $(\text{C}_8\text{H}_{10}\text{O}_8)_x + x \text{H}_2\text{O} \rightarrow x \text{C}_8\text{H}_{12}\text{O}_8$

*hydroxy acids* (hi drok s i e) Acids containing one or more hydroxyl groups in addition to the carboxyl group

EXAMPLE  $\text{CH}_2\text{CHOH COOH}$  lactic acid

*isomeric* (i so mer ik) Pertaining to compounds of the same percentage composition but having different structures and properties

EXAMPLE Sucrose and maltose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ )

*ketone* (ke tone) An oxidation product of a secondary alcohol

EXAMPLE  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$  acetone

*lipids or lipoids* A general name for fats and fat like substances

*mixed ether* Ethers in which the alkyl radicals are different

EXAMPLE  $\text{CH}_3-\text{O}-\text{C}_2\text{H}_5$  methyl ethyl ether

*monosaccharides* (mon-o sak ar ide) Carbohydrates which cannot be split into simpler saccharides

EXAMPLE  $\text{C}_6\text{H}_{10}\text{O}_5$   $\text{H}_2\text{O}$  or  $\text{C}_6\text{H}_{12}\text{O}_6$

*organic chemistry* Study of hydrocarbons and their derivatives

EXAMPLE  $\text{CH}_4$   $\text{CH}_3\text{Cl}$   $\text{CH}_3\text{OH}$

*peptide linkage* The  $\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad | \\ -\text{C}-\text{N}- \end{array}$  group sometimes called the biuret linkage

*phosphatids or phospholipids* (foa fa tids foa fo lip ids) Substituted fats containing phosphoric acid and nitrogen

EXAMPLE Lecithin

*polymer* (pol im-er) A compound formed by the process of polymerization

EXAMPLE Paraformaldehyde from formaldehyde

*polymerization* (pol im-er i-za shun) A reaction between like molecules with out loss of any atoms or groups of atoms

EXAMPLE  $\text{C}_2\text{H}_2$  to  $\text{C}_6\text{H}_6$   $\text{H CHO}$  to  $(\text{H CHO})_x$

*polysaccharides* (pol i sak'a rids) Carbohydrates containing several saccharide groups

EXAMPLE  $(C_6H_{10}O_5)_n$

*primary alcohol* An alcohol characterized by a  $-CH_2OH$  group

EXAMPLE  $R-CH_2OH$

*protein* (pro te in) Substances composed of H, C, O, N, and sometimes other elements that yield on hydrolysis amino acids or their derivatives

*saccharides* (sak a rids) The carbohydrates in the mono, di, and polysaccharides

EXAMPLE  $C_6H_{10}O_5$

*saponification* The process of a fat reacting with an alkali to form a soap

*saturated compounds* Compounds incapable of addition products

EXAMPLE Any member of the methane series

*secondary alcohol* An alcohol characterized by a  $CHOH$  group

EXAMPLE 
$$\begin{array}{c} R \\ \diagdown \\ \text{CHOH} \\ \diagup \\ R \end{array}$$

*simple ether* Ethers in which the alkyl radicals are the same

EXAMPLE  $C_2H_5-O-C_2H_5$ , ethyl ether

*simple protein* Compounds which upon hydrolysis yield amino acids or their derivatives

EXAMPLE Albumin

*soap* Metallic salts of fatty acids

EXAMPLE  $C_{17}H_{33}COONa$ , sodium stearate

*substitution products* Compounds formed by an element or a radical replacing another element or radical in a compound

EXAMPLE From  $CH_4$  forms  $CH_3Cl$  or  $CH_3OH$

*tertiary alcohol* (ter shi a re) An alcohol characterized by a  $COH$  group

EXAMPLE 
$$\begin{array}{c} R \\ \diagdown \\ \text{COH} \\ \diagup \\ R \end{array}$$

*unsaturated compounds* Compounds capable of forming addition products

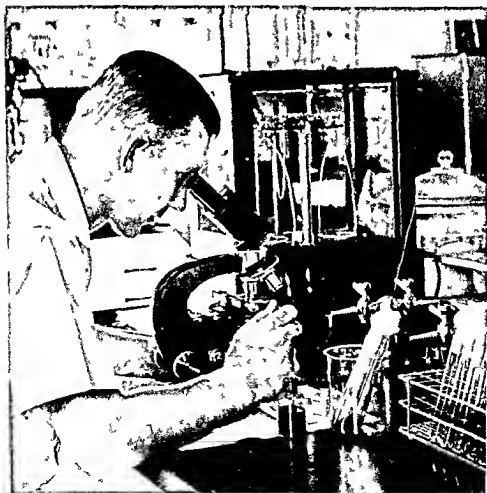
EXAMPLE Any member of the hydrocarbon series ending in ene

## **PART III**

# **BIOCHEMISTRY**

**A STUDY OF THE CHEMICAL CHANGES TAKING PLACE DURING LIFE PROCESSES**

*A Research Biochemist. Courtesy, Chas Pfizer & Co, Inc*



## INTRODUCTORY NOTES

### TO THE INSTRUCTOR

In this division of chemistry, known either as biochemistry or physiological chemistry, we shall take up a discussion of life processes in the light of the organic chemistry just studied. All living organisms perform the three main functions of (a) reproduction, (b) transformation of food into materials suitable for growth and repair, and (c) oxidation of these substances to furnish heat and energy so essential for the maintenance of life. In general, the subject involves a study of the chemical composition of living matter, the nature of the particular compounds of which this matter is composed, the chemical changes occurring during growth and decomposition, and the function of each of these substances. In particular, it deals with (1) the digestion of food, (2) the absorption of food products, (3) the blood as a circulating medium which carries nourishment to the cells and simultaneously carries their refuse to the excretory fluid.

This study enables the student to gain a better understanding of the chemical changes of normal living, of pathological living, and of the cause of disease as well as its diagnosis and treatment. In addition, biochemistry is the fundamental basis of the study of diet in all its ramifications including such applications as occur under the name of dietotherapy.

It is almost impossible in the presentation of biochemistry not to duplicate subjects studied in other courses, especially in physiology, diet and nutrition, and some aspects of medical nursing. These correlated subjects, however, may be presented from a different viewpoint in the chemistry course, and new chemical facts may be considered here not mentioned or stressed in other courses. The instructor will do well, however, to insist that all students review such subjects in their other texts, before coming to the chemistry class.

## OBJECTIVES

### 1. Facts and Principles:

- (a) To understand the function of the alimentary tract and how certain glands aid in this functioning.
- (b) To know the functions of the blood.
- (c) To learn the more important and generally accepted theories concerning the metabolic changes taking place in the tissue cells.
- (d) To study the urine, the chief excretory product of metabolism.
- (e) To understand the necessity of accessory food factors, whose absence leads to profound pathological changes.
- (f) To consider the activities of the endocrine organs which synthesize hormones that play an important role in regulating body processes.
- (g) To gain some understanding of the chemistry involved in physiology and nutrition.
- (h) To establish a relationship between the composition of chemical components of the body and the normal functioning of the tissues.

### 2. Attitudes:

- (a) To develop an appreciation of the physical basis of good health and the ways of preserving it.
- (b) To apply previously acquired knowledge of such allied sciences as zoology, bacteriology, pharmacology, and pathology and to correlate this with the modern understanding of the composition of the cell, the foodstuffs, and their relation to digestion and metabolism.
- (c) To build up a scientific attitude toward life processes.
- (d) To realize how a knowledge of chemistry broadens our interpretation of phenomena in everyday life.
- (e) To realize that biochemistry assists in our understanding of the composition of tissues and foods, and their general course of conduct in metabolism.

## THE CHEMISTRY OF DIGESTION

## CHAPTER OUTLINE

- |  |                                       |
|--|---------------------------------------|
| I FOODS                                  | (d) Coenzymes                         |
| (a) The purpose of foods                 | (e) Zymogen                           |
| (b) Necessity for digestion              | (f) Enzyme inactivation, anti enzymes |
| (c) Digestive fluids                     |                                       |
| II ENZYMES AS CATALYSTS                  | IV THE DIGESTIVE FLUIDS               |
| (a) Nature of enzymes                    | (a) Cooking vs digestion              |
| (b) Nature of enzyme action              | (b) Salivary digestion                |
| (c) Specificity                          | (c) Gastric digestion                 |
| (d) Classification                       | (d) Intestinal digestion              |
|  | (e) Bile                              |
| III BEHAVIOR OF ENZYMES                  | V. BACTERIAL DIGESTION AND ABSORPTION |
| (a) Properties of enzymes                | (a) Bacterial action in the colon     |
| (b) Effect of temperature                | (b) Absorption                        |
| (c) Effect of hydrogen ion concentration | (c) Feces                             |

## I. FOODS

## The Purpose of Foods:

Thus far, we have been considering the structure and the properties of three large classes of foodstuffs (carbohydrates, fats, proteins). These materials, in a general way, together with the vitamins, water, and mineral matter taken in with them, serve (a) to supply energy, (b) to build tissue, and (c) to prevent disease by regulating body processes. The ultimate object, however, in studying foods is not so much to learn their behavior in test tubes, but to investigate the chemical changes that these complex substances undergo after they enter the body.

## Necessity for Digestion:

The purpose of digestion is to prepare the food in such a form that the nutritional constituents may be taken up readily from the alimentary tract by the blood, leaving the undigestible residue to be excreted by the bowel. With the exception of such substances as the monosaccharides, the body is unable to utilize foods until certain chemical changes take place permitting them to pass through the membranes of the digestive tract. The resulting materials (nutrients) which are absorbed and carried to the tissues are generally not unaltered constituents, but transformed chemical

products arising from the action of the digestive juices on ingested foods

The so called *crystalloid foods* (p 110) are usually absorbed directly and unchanged, although the disaccharides such as sucrose first undergo hydrolysis to monosaccharides (p 338) *Colloidal foods*, such as starch, proteins and emulsified fats, are, on the other hand, not generally directly absorbable. The digestive fluids must disintegrate them into simpler chemical compounds before they can diffuse through the intestinal walls into the blood stream

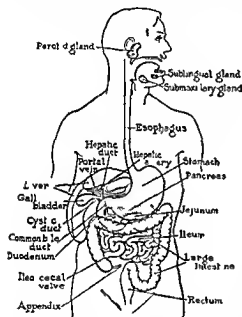


Fig 1—The Pathway of Food. The diagram indicates all organs of the digestive system. Why is food within the alimentary canal not considered to be within the body?

*Digestion is the process that takes place in the alimentary tract that results in the breaking down of complex foods into simple soluble compounds, whose molecules are small enough to pass through membranes and thus be absorbed by the cells of the body*

### Digestive Fluids

In changing the less soluble components of food into more soluble ones the colloids are for the most part converted into *crystalloids* by a group of catalysts (enzymes) derived from living cells. These enzymes are manufactured by special cells in the *salivary gastric pancreatic and intestinal digestive glands* and are secreted as dilute solutions into the alimentary canal



The chief chemical change involved in digestion is one of hydrolysis which is effected by enzymes in the acid or alkaline fluids secreted by the respective glands. In these hydrolytic changes, (a) the carbohydrates are changed to monosaccharides, (b) the fats to fatty acids and glycerol, and (c) the proteins to amino acids. Since enzymes have so much to do with the reactions which take place in the body, not only during digestion but also in many of the activities of the living cells, it is important to gain a clear idea of these mysterious catalysts and of their functions.

### SELF-TESTING QUESTIONS

1. What are the chief functions of foods?
2. What foods are included under crystalloids and which under colloids?
3. What is the purpose of digestion?
4. What are the digestive fluids?
5. What kind of chemical reaction is produced by enzymes?
6. What are the hydrolytic products of carbohydrate, fat, and protein digestion?

## II. ENZYMES AS CATALYSTS

### Nature of Enzymes.

In the study of chemical reactions we have been presented with instances in which the time required for a reaction was greatly reduced by the addition of a trace of some material which remained unaltered during the change taking place. Such materials which influence chemical changes without undergoing a change themselves are called *catalysts*. For example, in the chapter on carbohydrates, catalytic action was involved when starch was hydrolyzed into glucose, and cane sugar was converted to glucose and fructose, by boiling the starch or cane sugar solutions with a few drops of hydrochloric acid, *i. e.*, by increasing the hydrogen ion concentration of the solutions. In living bodies there is a great variety of chemical reactions produced in cells by organic catalysts. These catalysts, known as "enzymes" or "ferments," although made only by living cells, can exist and function quite separately from the cells making them, *i. e.*, isolated enzymes can act as catalysts in test tube reactions. The separation and purification of enzymes have met with great difficulty. To date, however, several enzymes of a protein nature have been obtained in a crystalline form—*urease*, which decomposes urea into ammonia and carbon dioxide, *pepsin* of the gastric juice, and *trypsin* of the pancreatic juice.

### Nature of Enzyme Action:

Enzymes, as organic catalyzers, aid in regulating a large number of the chemical reactions in the body. Not only is digestion a series of enzyme reactions but practically all of the other chemical processes that occur in the living body are catalyzed by enzymes. In studying the chemical nature of enzymes it seems conclusive that enzymes are proteins, and that the special property of a given enzyme is due most likely to a specific active group or groups in the enzyme molecule. The exact mechanism by which an enzyme catalyzes a chemical reaction is not clear but it appears that a temporary chemical combination between the enzyme and the substance being digested occurs. One molecule of an enzyme can catalyze the reaction of a very large number of molecules of the substance being digested.

### Specificity.

Enzymes differ somewhat from inorganic catalysts in their action. The enzymes for the most part exhibit a marked selective action for some substances and for this reason are limited in their action. For example, the enzyme that changes starch into sugar does not change cane sugar into a simpler sugar, but both starch and cane sugar undergo these changes in the presence of almost any dilute acid. Each enzyme has its own special action on one particular kind of substance which is called the *substrate* and so far as known only one such action. The action of each enzyme is analogous to a key which unlocks only a particular door. Only a few inorganic catalysts behave like enzymes in showing some degree of specificity.

### Classification

Since the chemical differences of enzymes are unknown, we can only classify them according to the kind of chemical action they bring about, and name them according to the nature of the substance acted upon.

For the different kinds of chemical changes produced by enzymes we have the following classes, (1) *hydrolytic enzymes*, which hydrolyze all foods in the course of digestion by accelerating the reaction between a large molecule (carbohydrate, fat, protein, or derivative) and water to form smaller molecules, (2) *fermenting enzymes*, which produce fermentation, (3) *oxidizing and reducing enzymes*, which yield body energy by the addition of oxygen or the removal of

## CLASSIFICATION OF SOME IMPORTANT ENZYMES\*

Type of Action	Enzymes and Distribution	Chemical Change
Hydrolysis	<b>Carbohydrases</b> Amylases Salivary amylase (ptyalin) Pancreatic amylase (amylolysin) <b>Disaccharidases</b> Sucrase Lactase Maltase	Starch $\rightarrow$ dextrins $\rightarrow$ maltose Starch $\rightarrow$ dextrins $\rightarrow$ maltose Sucrose $\rightarrow$ glucose + fructose Lactose $\rightarrow$ glucose + galactose Maltose $\rightarrow$ glucose + glucose
	<b>Lipases</b> Gastric lipase Pancreatic lipase	Fat (emulsified) $\rightarrow$ fatty acids + glycerol Fat (emulsified) $\rightarrow$ fatty acids + glycerol
	<b>Proteinases</b> Gastric proteinase (pepsin) Pancreatic proteinase (trypsin) Intestinal peptidases (erepsin)	Proteins $\rightarrow$ proteoses $\rightarrow$ peptones Proteins $\rightarrow$ proteoses $\rightarrow$ peptones $\rightarrow$ peptides $\rightarrow$ amino acids Peptones $\rightarrow$ peptides $\rightarrow$ amino acids
Fermentation	Zymase (yeast)	Monosaccharides $\rightarrow$ $C_2H_5OH + CO_2$
	Lactic acid (lactic acid bacteria)	Lactose $\rightarrow$ lactic acid
Oxidization	<b>Oxidases</b> Catalase Peroxidase	Decomposes $H_2O_2$ to form $O_2$ Liberates atomic oxygen from organic peroxides, favoring oxidation
Deaminization	<b>Deaminases</b> Urease	Urea $\rightarrow CO_2 + NH_3$
Coagulation	Rennin (gastric juice) Thrombin (blood)	Casein $\rightarrow$ paracasein (milk clot) Fibrinogen $\rightarrow$ fibrin (blood clot)

\* Hawk and Bergheim *Practical Physiological Chemistry* 10th ed., pp 235-6

hydrogen from the substances acted upon, (4) *deaminizing enzymes*, which release ammonia from organic amine groups, (5) *coagulating enzymes*, which produce coagulation of proteins such as rennin upon casein of milk

Each of the foregoing classes of enzymes is further subdivided into various members and named in accordance with the class of compound acted upon. Thus each of the hydrolytic enzymes acts on a specific substance, such as the carbohydrates, fats, proteins and their decomposition products. The ending *ase* to a word usually indicates an enzyme, and it is attached to the name of the substance that the enzyme acts on, called a *substrate*. Thus, the starch (*amylum*) hydrolyzing enzymes are called *amylases*, the fat (lipid) splitting enzymes *lipases*, and the protein splitting enzymes *proteinases*. When referring to a particular enzyme, it is customary to indicate its place of occurrence, *e.g.*, salivary amylase and pancreatic amylase. Since some of the enzymes—pepsin and trypsin, ptyalin, rennin—received names long before the adoption of the above mentioned method of classification there has been some confusion and disinclination or failure on the part of many to adhere strictly to the adopted nomenclature.

### SELF-TESTING QUESTIONS

- 7 What is the function of an enzyme?
- 8 Name three crystalline enzymes and give the function of each.
- 9 What is the chemical nature of an enzyme?
- 10 What is meant by the specificity of an enzyme?
- 11 Upon what basis are enzymes classified?
- 12 What are the various classes of enzymes and what are their functions?
- 13 What chemical change is produced by the hydrolytic enzymes on the different carbohydrates on the fats and on the proteins?
- 14 How are enzymes named?

## III BEHAVIOR OF ENZYMES

### Properties of Enzymes

Although widely distributed in living material, enzymes exist in such small amounts that their separation is quite difficult. However, several enzymes have been isolated as pure compounds which are of a protein character. Within recent years it has been learned that certain of the B complex vitamins act as the specific active group (*prosthetic group*) of some of the enzymes that function in

cellular oxidation and reduction reactions. Enzymes have certain properties in common. As they are relatively large molecules, they are colloidal in water, in dilute alcohol and in aqueous sodium chloride solution, but are precipitated by ammonium sulfate and strong alcohol. The large size of protein molecules accounts for the fact that enzymes do not readily diffuse through semipermeable membranes.

Although the structures of most enzymes are still unknown, there is available considerable knowledge of the factors that influence their activity.

### Effect of Temperature

Like most proteins, enzymes are very sensitive to heat and are inactivated at temperatures which coagulate protein ( $50^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ ). On the other hand, it is known that as temperature is increased the rate of chemical reactions is greatly accelerated. This generalization holds true of reactions catalyzed by enzymes. Therefore, in an enzyme reaction two opposing effects of temperature are involved, one the effect of increased temperature in increasing the rate of reaction and the other the effect of increased temperature in destroying the enzyme. The *optimum temperature* is that temperature at which an enzyme exhibits its greatest activity. In general this temperature is usually a few degrees above body temperature. At lowered temperatures such as  $0^{\circ}\text{C}$  the action of an enzyme is greatly decreased or may be almost completely inhibited.

### Effect of Hydrogen Ion Concentration (pH or acidity or alkalinity)

In addition to this influence of heat, enzymes are sensitive to the nature of the medium in which they exist. Some enzymes function only in the presence of dilute acids, and some only in dilute alkaline or neutral solutions. This is particularly true of pepsin which requires for its optimum action on proteins a definite hydrogen ion concentration corresponding to 0.2 to 0.5 per cent HCl, and above or below this approximate hydrogen ion concentration (pH of about 1.6) the action is inhibited. Trypsin on the other hand digests proteins in either a neutral or an alkaline medium (pH of 8.0), but is inactive in an acid solution. Furthermore, salivary amylase (ptyalin) is more active in a neutral than in either an acid or an alkaline medium, and is completely inactivated by the high hydrogen ion concentration of the gastric juice. There is an *optimum*

hydrogen ion concentration for maximum activity, the concentration depending upon the nature of the enzyme

### Coenzymes

Certain enzymes show activity and function properly only in the presence of other substances, generally called coenzymes. In some instances the factors necessary are inorganic ions. Calcium ion, for example, is essential for the activity of the prothrombin of the blood, and chloride ion speeds the activity of salivary amylase. Zymase of yeast requires the presence of phosphate ion. Such inorganic ions which are necessary for the functioning of certain enzymes are sometimes called *activators*.

Many active enzymes, particularly those involved in oxidations and reductions, have been found to consist of two parts, both organic, usually loosely bound together. One part, protein in character, is known as the *apoenzyme*, and the other portion a non-protein, is termed the *coenzyme* or *prosthetic* (helping) factor. In some cases these two parts can be separated by dialysis, and it is found that neither taken alone possesses enzyme activity. It is interesting to learn at this time that vitamins frequently enter into the structures of such coenzymes.

### Zymogen

The inactive state exhibited by certain enzymes is often referred to as the *zymogen* form or as the *proenzyme*. This inactive zymogen must be transformed or activated by certain specific substances (kinases) secreted by the cells. For instance, pepsinogen, the zymogen of the enzyme of the gastric juice, is activated by hydrochloric acid (secreted by the gastric cells) into pepsin, at a pH of 6.0 or below, and trypsinogen of the pancreatic juice is changed by enterokinase of the pancreatic cells into trypsin.

### Enzyme Inactivation, Antienzymes

In decided contrast to coenzymes which are needed for enzyme action, there are many organic and inorganic substances which inactivate enzymes, either reversibly or irreversibly. The salts of heavy metals such as silver, mercury, copper and lead, and in fact all the protein precipitants, are particularly toxic to enzymes. Other more specific organic inactivators that are formed by living cells are referred to as *antienzymes*. Such antienzymes occur in the lining cells of the digestive tract where their presence prevents

the digestion of the protein which forms the walls of the stomach and intestine. Antienzymes are also present in the blood and there is a reasonable amount of evidence to indicate that *in vivo* clotting of blood is prevented by antienzyme action. Enzymes are inactivated not only by heat, unfavorable hydrogen ion concentration (pH), and antienzymes, but also by shaking and ultraviolet light.

In a solution where enzyme action is occurring the activity of the enzyme usually decreases. This may be due to spontaneous decomposition of the enzyme or to the effect of accumulation of end products of the reaction. Enzymes do not change the equilibrium point of a reaction but merely cause the equilibrium point to be attained more rapidly. Therefore the speed of the reaction will decrease as the equilibrium point is reached.

### SELF-TESTING QUESTIONS

- 15 What facts seem to indicate the colloidal nature of enzymes?
- 16 What factors influence the activity of enzymes?
- 17 Illustrate by example what is meant by *optimum temperature*.
- 18 What are coenzymes?
- 19 What is a zymogen?
- 20 What are antienzymes?
- 21 How do salts of heavy metals inactivate enzymes?
- 22 What other substances inactivate enzymes?
- 23 How do enzymes as catalysts differ from inorganic catalysts?

## IV. THE DIGESTIVE FLUIDS

With some understanding of the nature of enzymes we are ready to consider the changes that foods undergo in the course of digestion. To some extent this is a familiar story, since the physiology of digestion has been or will be presented in another course. As a consequence, the discussion in this chapter will be more concerned with the chemical factors involved in digestion.

### Cooking vs Digestive Processes

Before considering the different digestive fluids, attention is called to the fact that many processes involved in the preparation of food are somewhat similar to those of digestion. Prolonged cooking in a slightly acid medium may partly hydrolyze starch and disaccharides into simple sugars. Moreover, cooking prepares raw starch food for more effective enzyme action in the body by rupturing the insoluble cellulose coating which surrounds the starch granules. Cooking converts the tough white fibrous connecting tissue (e.g., collagen) of meat into gelatin. In addition, the heat required to

## DIGESTIVE FLUIDS

Site	Secre- tion	Enzyme	Substrate	Medium	Extent of Digestion	Products Formed
Mouth	Saliva	Ptyalin	Starch	Usually slightly acid about pH 6.5	Slight	Dextrin → maltose
Stomach	Gastric	Pepsin	Proteins	Normally about pH 1.6  0.2% HCl	Incom- plete	Proteoses and peptones
		Rennin  Lipase	Casein  Fats (emulsi- fied)		Mostly complete Very slight	Paracasein  Fatty acids + glycerol
Intestine	Pancre- atic	Trypsin Chymo- trypsin Carboxy- pepti- dase	Proteins Proteoses Peptones Peptides	About pH 7.8  0.5% Na <sub>2</sub> CO <sub>3</sub>	Almost complete	Amino acids
		Amylopsin	Starch		Almost complete	Amino acids
		Steapsin	Fats		Almost complete	Dextrins maltose Fatty acids + glycerol
					Almost complete	
	Intes- tinal Mucosal cells	Amino- pepti- dase	Polypep- tides		Complete	Amino acids
		Dipepti- dase				
		Maltase	Maltose		Complete	Glucose
		Sucrase	Sucrose		Complete	Glucose + fructose
	Bile	Lactase	Lactose		Complete	Glucose + galactose
		No en- zymes, action due to salts, etc	Fats			Emulsifies fats Promotes fat ab- sorption



cook foods, especially meats, destroys pathogenic microorganisms which in some cases may cause serious disturbances in the body. Storage, too, brings about chemical changes in the composition of foods, and meats kept at certain temperatures become more tender through the action of the natural enzymes in the meat slowly changing and softening the structure of connective tissue that holds the muscle fibers together, a process taking place in from four to eight weeks \* Some fruits and vegetables kept in storage also ripen through the action of enzymes. It is quite evident, then, that the preparation of foods often corresponds to, or is supplementary to, digestive processes. Cooking requires a much higher temperature to produce changes in food corresponding to those brought about by digestive enzymes at body temperature. This has at least one drawback. Prolonged cooking is associated with partial or complete destruction of some of the vitamins, notably vitamin C (antiscorbutic) and may destroy some of the delicate flavor of certain types of food. However such a simple thing as putting a cover on the vessel in which vegetables are boiled excludes the air and consequently prevents much destruction of vitamin C.

### Salivary Digestion.

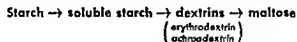
The saliva is secreted by three pairs of large glands, the parotid, the submaxillary, and the sublingual and includes the secretion of numerous small glands that are present in the lining of the oral cavity. Saliva contains over 99 per cent water and less than 1 per cent solids. The chief solid is mucin, which is a glycoprotein that renders the saliva viscous and ropy and accounts for its lubricating action. Other solids include the enzyme salivary amylase (ptyalin), and inorganic and organic substances that are derived from the blood. The inorganic salts of saliva have two important functions—the phosphates act as buffers that tend to maintain the reaction ( $pH$ ) of the saliva constant, and the chloride ions are essential as coenzymes for the salivary amylase.

The flow of saliva (about 1500 ml daily) is the result of stimulation of the salivary glands by the nervous system, as is evidenced by the fact that actual contact with food is unnecessary since sight, odor, or even thought will cause the salivary glands to secrete profusely.

\* The Tenderay Process Sterilamps accomplish this result in one to two days by keeping the meat free from bacterial action of the air at a temperature of 60° F and a humidity of 90.

Other factors which influence secretion are the nature and quantity of the foods eaten, and the thoroughness of mastication

**SALIVARY AMYLASE OR PTYALIN** is the principal enzyme of the saliva. This enzyme is capable of hydrolyzing cooked starch into dextrins and maltose



The maltose so produced is later hydrolyzed by intestinal maltase to glucose

As foods are usually masticated only for a relatively short time before they are swallowed very little digestion of starch takes place in the mouth. Fortunately, salivary digestion may proceed for some time, 10 to 20 minutes or even longer, after reaching the stomach, owing to the time required for the food in the stomach to become mixed with the acid gastric juice. This acid medium eventually inhibits any further action of the salivary enzymes. The main function, then, of the saliva is to begin hydrolysis of cooked starch into dextrins and maltose. In addition, saliva keeps the mouth moist, and dissolves and lubricates some of the masticated food, whose juices stimulate the taste buds, thus making food more palatable

### Gastric Digestion

The food upon passing through the esophagus enters into the fundus of the stomach, a hollow muscular pouch, whose lining is a soft mucous membrane arranged in folds. It is in these folds that the glands are found which secrete gastric juice (2000 to 3000 ml

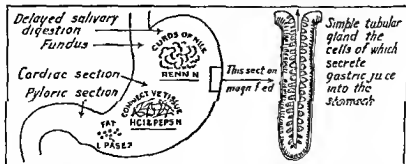


Fig 2—Where Gastric Juice Is Produced Over 2 000 000 tube like glands secrete gastric juice Where does the digestion of starch stop and that of protein begin?

daily), a thin, watery, strongly acid (0.2 to 0.5 per cent HCl) solution. Gastric juice contains *gastric proteinase* or *pepsin*, a protein splitting enzyme, *rennin*, a milk coagulating enzyme, and traces of gastric lipase, a fat splitting enzyme (Fig. 2).

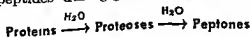
The gastric glands (fundus and pyloric), like the salivary glands, are stimulated by *psychical* and chemical action. The *psychical* form of stimulation is mainly pleasurable anticipation, which causes a rapid flow of gastric juice, while strong mental or physical activity, such as anger or excitement retards its flow. The chemical stimuli may be produced by *certain substances*, particularly the soluble extractives of foods. As the extractives of meat are quite effective in this respect we may understand the value of beginning a meal with a clear soup as an appetizer.

The formation of the hydrochloric acid in the gastric juice is closely associated with the parietal cells of the gastric glands. The chloride ions of the hydrochloric acid probably come from the sodium chloride in the blood and the hydrogen ions perhaps from some weak acid such as carbonic acid. One prevailing theory is that hydrochloric acid forms as the result of an interchange of ions between sodium chloride and carbonic acid, as indicated in the following equation:



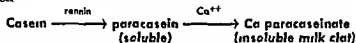
The concentration of the acid secreted is fairly constant (0.2 to 0.5 per cent). If the percentage of acid is below normal (hypoacidity) as may occur in pernicious anemia and cancer of the stomach, digestion is retarded. Furthermore, in hypoacidity, there is less check on the growth of the microorganisms in the stomach. The hydrochloric acid is secreted largely after the food enters the stomach, and then it comes into contact with the food. Occasionally, the secretion of hydrochloric acid is above normal (hyperacidity). In peptic ulcer patients there is often hyperacidity, a condition closely associated with emotional strain and overwork.

PEPSIN or gastric proteinase is produced as an inactive zymogen (pepsinogen) by the chief cells of the gastric glands. When the pepsinogen comes in contact with the acid produced by the parietal cells it is activated and converted into pepsin. This enzyme acts on most of the proteins of the ingested foods and converts them into soluble proteoses. Some proteoses may change to peptones or even to higher polypeptides during gastric digestion.



This partial hydrolysis of the proteins in the stomach is of great importance in that the proteinases of the pancreatic and intestinal secretions are able to act more quickly and completely in furthering digestion of the proteins in the small intestine

RENNIN is the enzyme in the gastric juice of young animals which splits the casein molecule of milk into two smaller molecules, called paracasein, each of which unites with a calcium ion to form insoluble calcium paracaseinate. This insoluble formed protein digests more readily than colloidal casein and furthermore, prolongs the digestive action of pepsin, the chief proteinase of the stomach.



Attention is especially called to the fact that rennin can clot milk in a *neutral* solution, an important property in the digestion of milk in unweaned babies. Curdling of milk may also be produced by acids or by the action of pepsin.

Gastric lipase, a fat splitting enzyme, is of but slight importance, largely because of the presence of hydrochloric acid, which is unfavorable for the emulsification of fat and the action of the enzyme. Some fatty acids and glycerol are probably formed as the result of the hydrolysis of emulsified fats such as those occurring in milk and egg yolk.

In two or three hours the combined effect of the proteolytic enzyme, hydrochloric acid, and the churning of the wavelike contractions of the stomach convert the food into a thin watery liquid, called *chyme*. It is in this way that muscle fibers and the connecting tissues of meat (in the presence of acid) absorb sufficient water to cause them to swell, soften and become more accessible to further digestion by the enzymes.

Following the action of the enzymes and the formation of *chyme*, peristaltic contractions propel this material forward toward the pylorus. Succeeding peristaltic waves force this semiliquified food through the opening of the pylorus into the small intestine. The acid is immediately neutralized by alkaline intestinal juices, reflexes occur, and the pyloric opening closes. Recent opinions on the discharge of food from the stomach seem to favor the view that many factors control this process rather than that either the hydrochloric acid or the state of the digestive products alone governs this action.

### Intestinal Digestion:

The liquid food (chyme), upon leaving the stomach, enters the duodenum which is the first 11 or 12 inches of the small intestine. From a digestive standpoint the duodenum is the most important part of the intestine. Here, the chyme is acted upon by three



Fig 3—Avoiding Guesswork. Doctor fluoroscopes patient's digestive tract with aid of x ray unit. What salt makes this examination possible? Courtesy, General Electric Co

juices the *bile*, the *pancreatic juice*, and later, by the *intestinal juice* (*succus entericus*) The acid chyme is neutralized on entering the intestine and when the food is sufficiently alkaline the action of the digestive enzymes of the intestinal juices begins The acid food upon contact with the intestinal mucosa reacts with prosecretin elaborated by the duodenum cells to form secretin, a hormone which enters the blood stream and stimulates the pancreas to secrete the pancreatic juice Simultaneously, bile flows into the duodenum

**PANCREATIC JUICE** This secretion (500 to 800 ml daily) is a clear, watery, alkaline (pH 7.5 to 8 or 0.5 per cent  $\text{Na}_2\text{CO}_3$ ) solution, much like saliva, but far more important than either the salivary or the gastric secretions Pancreatic juice contains several important enzymes *trypsin*, a protein splitting enzyme, *chymotrypsin*, a milk clotting and protein splitting enzyme, *carboxypeptidase*, which hydrolyze peptides to amino acids, *amyllopsin* or pancreatic amylase, a starch splitting enzyme, and *steapsin* or pancreatic lipase, a fat splitting enzyme

1 *Trypsin* or pancreatic proteinase appears in its inactive form (*trypsinogen*), which is readily converted into the active trypsin by a substance called *enterokinase* According to the present view, enterokinase is an enzyme that occurs in the secretion of the walls of the duodenum, acts upon trypsinogen as a substrate, and converts it into trypsin Trypsin is an important enzyme of the pancreatic juice, and is much more effective than pepsin upon the proteins, because trypsin not only catalyzes native protein hydrolysis, but also continues the hydrolytic process to the amino acid stage

Proteins  $\rightarrow$  proteoses  $\rightarrow$  peptones  $\rightarrow$  polypeptides  $\rightarrow$  peptides  $\rightarrow$  amino acids

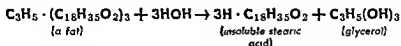
2 *Chymotrypsin* is secreted in the pancreatic juice as an inactive zymogen, *chymotrypsinogen*, which is activated in the duodenum by trypsin The active enzyme has an action very similar to trypsin but in addition has a powerful milk clotting activity

3 *Carboxypeptidase* This peptidase of the pancreatic juice catalyzes the hydrolysis of certain peptides to amino acids

4 *Amylopsin* or pancreatic amylase, the starch-splitting enzyme, has an action similar to salivary amylase (*ptyalin*) Amylopsin not only changes any starch incompletely acted upon by salivary amylase into maltose, but it is capable of digesting uncooked starch

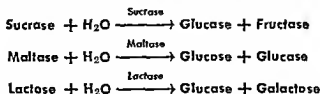
Starch  $\rightarrow$  dextrins  $\rightarrow$  maltase

5. *Steapsin* or pancreatic lipase, the most important fat-splitting enzyme, has the power of hydrolyzing neutral, emulsified fats to glycerol and insoluble fatty acids.



There is no marked difference between the digestibility of animal and vegetable fats. The percentage of digestibility of edible fats follows: vegetable fats 97.1 per cent, butter and lard 97 per cent, animal fats 96 per cent, and hydrogenated vegetable oils 93.5 per cent. The emulsification of fat and the consequent hydrolysis of the fats are greatly accelerated by the bile salts.

**INTESTINAL JUICE:** The intestinal juice represents the combined secretion of the glands which line the walls of the small intestine. It was formerly believed that this secretion had a strong digestive action since preparations of ground intestinal mucosa possessed powerful disaccharide splitting enzymes and also peptidase activity. However, at present, authorities feel that these enzymes are located inside of the cells of the intestinal wall and are never present in appreciable amounts in the secretion of the intestine. The digestive action of these enzymes is exerted as food passes through cells of the intestinal wall in the process of absorption. The disaccharide splitting enzymes include sucrase, maltase and lactase which catalyze the following reactions:



The completion of protein digestion is also accomplished by the action of several intracellular peptidases (known collectively as erepsin) which include at least two different enzymes, aminopeptidase and dipeptidase. The end products of protein digestion are amino acids.

The fact that the secretion of the intestinal wall does not contain large quantities of enzymes should not be reason to regard it as unimportant since it also has an important function in neutralization and lubrication.

## SELF-TESTING QUESTIONS

- 24 Name the salivary glands
- 25 Discuss the composition of saliva
- 26 What produces a flow of saliva?
- 27 Name the salivary enzymes and their functions
- 28 Name and state the function of each enzyme in the gastric juice
- 29 How does hydrochloric acid of the gastric juice influence digestion?
- 30 What is chyme?
- 31 What is the function of secretin?
- 32 Name the pancreatic enzymes and their functions
- 33 What is the function of each intestinal enzyme?

## Bile

Bile is a viscous yellow to brown, bitter tasting alkaline fluid, that is secreted (500 to 800 ml daily) by the liver and flows *via* the bile ducts into the duodenum. The rate of secretion and of flow of bile is influenced by the nature of the food undergoing digestion, the stimulation probably being influenced by a hormone, secretin. Many salts such as Epsom salts stimulate the flow of bile. In the absence of food, most of the bile is diverted to the gallbladder (about 30 ml capacity) where it is stored and becomes concentrated to one tenth its previous volume by lymphatic reabsorption of water, salt, cholesterol, and pigment from it and by the addition of mucin, a secretion from the wall of the gallbladder. During active digestion the contents of the gallbladder are evacuated into the duodenum and thus provide a concentrated supply of bile. The bile may also be considered an excretion, since it eliminates, as waste products of cellular action, certain substances which it alone can dissolve (*e g*, cholesterol). In addition to the lipids, mucin, and bile pigments, bile contains certain salts, the importance of which will be discussed.

The following table shows the common constituents in bile

<i>Secretion Components</i>	<i>Excretion Components</i>
Bile salts Sodium hydrogen carbonate Water	Bile pigments Cholesterol

**THE BILE SALTS OR BILE ACIDS** Although bile contains no digestive enzymes it plays an important role in the digestion and absorption of fat and indirectly that of other foodstuffs. As it is



alkaline, the bile along with the pancreatic juice and intestinal juice neutralizes the acid chyme from the stomach. As already mentioned the bile contains a type of compound called bile salts or bile acids. The two most important of these substances are sodium glycocholate and sodium taurocholate. A most important property of the bile salts is that they act as wetting agents by lowering surface tension of water, and in so doing give greater penetration, and facilitate the emulsification of fat. In the absence of adequate emulsification very little fat digestion by pancreatic lipase (steapsin) occurs in the intestine.

In addition the bile salts play an important role in fat absorption by uniting with the insoluble fatty acids, liberated from fats by lipase action, to form soluble compounds known as choleic acids. These choleic acids upon absorption separate again, and the fatty acids unite with glycerol in the lymphatic vessels of the villi (lacteals) to form fats which are transported by the lacteals to the thoracic duct and eventually to the blood stream. The liberated bile salts are then available for further use by the liver. They are resecreted into the bile and thus undergo a type of circulation—i. e., from blood, to liver, to bile, to intestine and back to blood.

The bile salts possess the property of stimulating the secretion of bile and as such can be regarded as cholagogues (substances stimulating the flow of bile). They also aid peristalsis. In the absence of adequate bile flow extensive putrefaction of protein occurs in the lower portion of the gastrointestinal tract. This is due in part to the decreased peristalsis and in part to the undigested fat which forms an oily film over protein particles and retards their digestion. Thus the absence of bile causes serious disturbances of intestinal digestion and absorption. The feces contain greatly increased quantities of fat and may be clay colored and greasy, and have a very foul odor. In some cases constipation may result from decreased peristalsis.

**THE BILE PIGMENTS** These consist mainly of *bilirubin* and *biliverdin*, mostly\* formed when the liver salvages "organic iron" from the blood pigment (hemoglobin) of worn out red blood cells. In this decomposition of hemoglobin into globin and hematin, the latter, with loss of iron, changes into bile pigments which impart a yellow to brown color to bile. Bilirubin has a reddish cast, while its oxidized product, biliverdin, is a green pigment. Normally

\* Bile pigments may be formed in other tissues, e. g., spleen, bone marrow lymph glands

there is little or no biliverdin in the bile but on exposure of bile to air it will turn green because of oxidation of bilirubin to biliverdin. Oxidation produces a series of colored compounds, including bilicynin, a blue pigment. The series of colors in bruised skin is undoubtedly due to the decomposition of the hemoglobin liberated by injured red cells which exuded from the capillaries of the injured tissue. Obstruction to the bile ducts, disease and dysfunction of the liver or an abnormal destruction of the red blood cells will result in an increased amount of bilirubin in the blood. This will diffuse into the skin and mucous surfaces and will give them a characteristic yellow color which is known as jaundice or icterus.

In the intestines, the reducing bacteria change bile pigments in part to *stercobilin*, a brown pigment, which accounts for the characteristic color of feces. Some urobilin is also formed, and a part of the yellow color of urine is due to this pigment. It is of secondary importance to another yellow pigment in urine called *urochrome*. Too frequent elimination (diarrhea) does not allow for much reduction of bile pigments with the consequence that feces then have a decided yellow instead of a brown color, the color depending somewhat on the cause of the diarrhea.

**CHOLESTEROL** This important excretory compound of the bile is ordinarily soluble in bile. However, in the presence of foreign substances, such as injured cells or bacteria, the cholesterol tends to crystallize, carrying with it some bile salts and pigments to form gallstones. It may also play a part in arteriosclerosis. Cholesterol is an alcohol ( $C_{27}H_{45}OH$ ) and like glycerol ( $C_3H_5(OH)_3$ ) unites with fatty acids to form esters but it differs in that its esters do not easily saponify. When cholesterol deposits on the inner surface of blood vessels, hardening of the arteries occurs. Lanolin, the fat of sheep's wool, contains the stearic, palmitic, and oleic acid esters of cholesterol.

### SELF-TESTING QUESTIONS

- 34 What is bile?
- 35 What stimulates the flow of bile?
- 36 Why may bile be called an excretion?
- 37 What are the functions of the bile?
- 38 How does the absence of bile affect digestion?
- 39 What are the two chief bile pigments?
- 40 What are the functions of sodium glycocholate and sodium taurocholate?

## V. BACTERIAL DIGESTION AND ABSORPTION

### Bacterial Action in the Colon:

Following intestinal digestion any undigested, unabsorbed food is forced into the large intestine, or colon, where it is subject to the action of bacteria. A small amount of material may be absorbed here, but there are no secreting glands to produce further digestion.

Ordinarily, most of the bacteria in food are killed by the acid chyme of the gastric juice. However, upon reaching the more alkaline fluids of the intestine, neutralization of the acid takes place and a medium favorable for the growth of bacteria is produced. Normally in the lower part of the small intestine and in the large intestine an enormous number of bacteria are found. Some idea of the number can be imagined when it is realized that more than one fourth of the weight of dried feces consists of dead bacteria.

There are many kinds of bacteria in the colon and the chemical changes which occur depend largely upon what material they act upon. In other words, diet may regulate intestinal putrefaction. For instance, to reduce *putrefaction* the amount of protein is reduced and carbohydrates are increased. Whenever this is done the bacteria act upon the carbohydrates to produce acids which are unfavorable to putrefaction. Advantage is taken of this fact in the use of buttermilk, sour milk, and acidophilus milk to reduce in intestinal putrefaction. To reduce *fermentation*, proteins are largely substituted for carbohydrates. In this way, very little undigested carbohydrates reach the colon for the action of the fermentative bacteria. Ordinarily, the greater the cellulose, hemicellulose, etc., content of the diet, the greater will be the amount of indigestible carbohydrate residues reaching the colon.

Of recent and decided interest is the discovery that bacterial action depends largely upon the medium, and if the medium contains sufficient carbohydrates, no toxic putrefaction products are formed. For instance, the diphtheria germ in the presence of sufficient lactose merely changes lactose into lactic acid, but in the absence of certain carbohydrates, the same bacterium develops the dread diphtheria toxin.

Carbohydrates are readily attacked by certain bacteria to form relatively nontoxic substances, such as acids (lactic and the lower fatty acids of the butyric acid type), alcohol, and gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ). Cellulose, such as that of young celery, is acted upon to

some extent by bacteria to produce compounds, which may be absorbed

Bacteria in the intestine perform the useful function of decomposing indigestible residues and perhaps in aiding the synthesis of certain water soluble vitamins notably the B vitamins. Quantities of vitamin K sufficient to meet the needs of the body are also synthesized by intestinal bacteria.

Fats do not appear to be acted upon by bacteria, or at least not to any appreciable extent. It is possible that some fatty acid and glycerol may be formed by bacterial decomposition of fats.

Protein decomposition by bacteria yields amino acids, which further decompose by first splitting off ammonia (deamination) and then carbon dioxide (decarboxylation) to form certain phenols from aromatic amino acids, or the amino acids may only split off carbon dioxide and immediately produce more toxic amines. Histamine, phenol, indole and skatole are some of these decomposition products the latter two contributing to the characteristic and disagreeable odor of feces.

The derived phenols, acids and amines resulting from bacterial action are toxic when absorbed in excess of the amount that can be detoxicated by the liver and eliminated via the kidneys as harmless compounds. Hitherto, the prevailing opinion was that during constipation these putrefaction products are absorbed and are responsible for such ills as headaches, irritability, and general malaise. This does not seem entirely warranted in the light of experimental evidence. These auto-intoxication symptoms may be produced by abnormal distention of the lumen of the rectum as when the rectum is packed with cotton. The acceptance of this statement seems to be warranted when we consider that evacuation of the colon following constipation gives relief from these symptoms in certain uncomplicated cases. The prompt relief within a few minutes following evacuation suggests that the disturbance was partly of a nervous origin. Eliminating the toxic materials from the body would require a much longer time.

These observations along with the recognition that certain important vitamins may be synthesized and contributed to the body's economy by intestinal bacteria have caused a considerable shift in attitude regarding the usefulness or harmfulness of intestinal bacteria. In general at the present time it is felt that they do perform useful functions and that it is only when there is a disturbance of function or a diseased state that they produce undesirable effects.

## Absorption:

No absorption of food takes place in the mouth and but very little from either the stomach or the colon. From the colon, water and some salts are absorbed, the absorption of the water accounting for the consistency of the feces. Practically all absorption of food takes place in the small intestines, which are particularly well adapted for this purpose by reason of their great length (about 25 feet), because of the long time foods remain in the intestine (about five hours; sometimes several days), and the large exposed surface (about 100 square feet).

The vascular projections in the intestinal walls are known as villi. They afford an extraordinarily large surface, and, with their rich and rapidly circulating supply of blood and lymph, they permit quick absorption of digested food materials (Fig. 4).

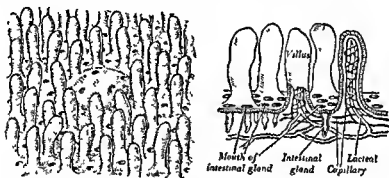


Fig. 4—How Food Enters the Blood. The villi absorb digested proteins and carbohydrates. Digested fat enters the lacteals and lymph. If each villus were a pit, like an intestinal gland, how would the rate of absorption be altered? From "Biology for Today," Ginn & Co

**Carbohydrates**, as monosaccharides, are readily absorbed and carried by the blood to the liver. Here they are largely converted to liver glycogen which as a reserve of carbohydrate gradually breaks down to maintain constant levels of blood sugar.

**Fats**, as already mentioned, are emulsified and hydrolyzed to form fatty acids and glycerol, the glycerol being readily absorbed in the epithelial cells of the villi, while the insoluble fatty acids are probably absorbed as complex compounds (choleic acids) formed by the addition of *bile acids and fatty acids*. The glycerol and fatty acids reunite to form fats, which pass from the epithelial cells to the lacteals, and in lymph to the blood, and thence to the tissues.

*Proteins* are absorbed in the form of amino acids. A part of the amino acids is used to build tissue protoplasm and a part is oxidized to urea, carbon dioxide, and water with the formation of energy. Before amino acids are oxidized they must first be deaminized (pp. 417, 521); this process of splitting off ammonia takes place in the liver. It sometimes happens that traces of unchanged proteins (native), and probably partly decomposed proteins, are absorbed from the intestines following the ingestion of certain foods which act immunologically on the system. Such food idiosyncrasies are peculiar to certain individuals, and often follow the eating of strawberries, eggs, and certain other food proteins. Sensitiveness to food proteins has been held responsible for some forms of allergy,\* including asthma, and certain skin eruptions

### SUMMARY OF FOOD ABSORPTION

<i>Food</i>	<i>Absorbable Food Compound</i>	<i>Place of Absorption</i>	<i>Route in Circulation</i>	<i>Food Products Carried by the Blood</i>
Carbohydrates	Monosaccharides	Blood vessels of villi. Rectum or any part of the gut as in intestinal obstruction	Blood of portal vein to the liver	Glucose (part of the glucose absorbed and that formed from the fructose and galactose is changed by the liver into glycogen. Other tissues may form glycogen)
Fats	Glycerol Fatty acids	Epithelial cells of villi	Lacteals to lymphatics, to left thoracic duct, to blood	Emulsified fat, the absorbed glycerol, and fatty acids having been reunited in the cells of the mucosa
Proteins	Amino acids	Blood vessels of villi	Blood of the portal vein to the liver and to other tissues	Amino acids

\*Allergies are unusual reactions to any substance. They may be caused by foci of infection, by the foods we eat, or by things we touch or inhale. Also allergy patients may become sensitive to intangible agents such as sunlight, heat, cold and pressure.

*Inorganic salts*, especially those containing sodium, potassium, and chloride ions are readily absorbed through the intestines, but some ions such as magnesium and sulfate ions undergo very little absorption, and are more likely to withdraw water from the tissues by osmosis, a fact emphasized in the laxative action of Epsom salts ( $\text{MgSO}_4$ )

The absorption of calcium and phosphorus ions is largely due to the presence of the antirachitic vitamin D

## The Feces

The gastrointestinal tract represents a pathway of excretion for the body. It has already been mentioned that bilirubin and cholesterol are excreted into the intestine through the bile. In addition a certain amount of excretion of waste substances is carried out by the mucosa of both the small intestine and the large intestine. The feces also contain undigested, indigestible, and unabsorbed food residues along with residues of the gastrointestinal secretions (digestive juices). The waste substances of food include indigestible cellulose from carbohydrates, undigested connective tissue from meat proteins and undigested fats. This complex mixture provides an ideal medium for the growth of *microorganisms* and actually in the cecum and colon are found enormous numbers of bacteria of various types. It has been estimated that as much as half of the bulk of the stool may be due to the bodies of dead and living bacteria.

The composition of the feces will vary greatly depending on the ratio of the various constituents mentioned. In diseases of the pancreas and liver, where there is a deficient flow of pancreatic juice and bile digestion in the intestine is impaired and large quantities of fat and protein appear in the stool.

Normally there is no blood in the stool but if a lesion is present in the gastrointestinal tract, blood can usually be detected. If the bleeding is in the lower colon or rectum the blood can be recognized as such. However, if the bleeding is higher, such as may occur in peptic ulcer or in carcinoma of the intestine, the blood is altered and is referred to as occult (hidden) blood. If the quantity of occult blood is large the stools will have a black, tarry appearance which is quite characteristic but if the amount is small it is necessary to employ a chemical test (such as the benzidine test) for the identification of the blood.

## SELF-TESTING QUESTIONS

- 41 What action takes place when food enters the colon?
- 42 Does digestion take place here? Explain
- 43 How is the putrefying action of bacteria reduced?
- 44 The production of acids in the colon has what effect?
- 45 What products are formed by bacteria acting upon carbohydrates?
- 46 How do bacteria act upon proteins?
- 47 What is the effect of the absorption of putrefactive products?
- 48 What may cause symptoms of autointoxication?
- 49 What is the relation between carbohydrates and toxic putrefactive products?
- 50 In what way may cellulose be made available to the body?
- 51 Where are foods absorbed?
- 52 What happens to the carbohydrates after absorption?
- 53 In what form are fats absorbed?
- 54 What is the effect produced by the absorption of protein (unchanged protein)?
- 55 What components of foods resist digestion?
- 56 What significance is attached to finding large quantities of fat and protein in the feces? of blood?

## SUGGESTED ACTIVITIES

### I THOUGHT PROVOKING QUESTIONS

- 1 The fact that enzymes are inactivated by alcohol salts of heavy metals and heat shows what classification of an enzyme?
- 2 What is there about the nature of sugars and mineral salts which permits them to be absorbed directly while starches fats and proteins must be changed in order to be absorbed?
- 3 Why does it require a much higher temperature to oxidize sugar outside the body than it does inside?
- 4 How does the appearance of food indirectly aid digestion?
- 5 Enumerate the possible functions of hydrochloric acid in the stomach
- 6 What useful purpose do the bacteria in the colon serve?
- 7 Why are the small intestines well adapted for the absorption of food?
- 8 Where and in what forms are the various foods absorbed?
- 9 In what forms are the foods carried by the blood?
- 10 In what ways does trypsin differ from the action of pepsin pepsin differs from pepsin and amylase from ptyalin?
- 11 What hydrolytic changes in foods are produced by the digestive fluids?
- 12 How are the bile salts supposed to function?
- 13 What conditions may cause bile constituents to be increased in the blood?
- 14 How do you account for the series of colors in a bruised skin usually called 'a black and blue spot'?



- 15 Considering that milk contains lactose, fat, the proteins, water, and inorganic salts, state the action which takes place in the passage of milk along the alimentary canal

## II VOCABULARY TESTING OF NEW TERMS

enzyme	digestion	hormone	steapsin
coenzyme	ptyalin	trypsin	peptidase
antienzyme	pepsin	enterokinase	bile
zymogen	rennin	amylopsin	cholesterol
apoenzyme	secretin		

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 The Chemical Makeup of the Body Cells
- 2 Enzymes as Catalysts
- 3 The Nature of the Body Enzymes

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 735, 737, 739

## THE CHEMISTRY OF BLOOD AND LYMPH

## CHAPTER OUTLINE

- |   |  |
|---|--|
| <p><b>I BLOOD</b></p> <p>(a) Characteristics of blood</p> <p>(b) Functions of blood</p> <p>(c) Composition of blood</p> <p><b>II FORMED ELEMENTS</b></p> <p>(a) Erythrocytes or red cells</p> <p>(b) Leukocytes or white cells</p> <p>(c) Platelets</p> <p>(d) Clotting of blood</p> <p><b>III ACID-BASE BALANCE OF THE BLOOD</b></p> <p>(a) Constancy of blood reaction</p> <p>(b) Hydrogen ion concentration</p> <p style="padding-left: 20px;">pH</p> <p>(c) Proteins as buffers</p> <p><b>IV BLOOD CHEMISTRY</b></p> <p>(a) Tests for blood</p> <p>(b) Blood groups and transfusion</p> <p>(c) Rh factor in blood</p> <p>(d) Collection and preservation of blood</p> | <p>(e) Blood analysis as an aid in diagnosis and prognosis</p> <p><b>V PLASMA</b></p> <p>(a) Function of plasma</p> <p>(b) Function of the plasma proteins</p> <p>(c) Other plasma constituents</p> <p><b>VI FUNCTIONS OF THE BLOOD</b></p> <p>(a) Transportation of nutrients and oxygen</p> <p>(b) Transportation of waste products</p> <p>(c) Transportation of hormones</p> <p>(d) Diffusion of heat</p> <p>(e) Defensive action of the blood</p> <p>(f) Other blood constituents</p> <p>(g) Tissue oxidation</p> <p><b>VII EXTRACELLULAR WATER AND LYMPH</b></p> <p>(a) Functions of lymph</p> <p><b>VIII ANTIBIOTICS AND SULFA DRUGS</b></p> |
|---|--|

## I. BLOOD

## Characteristics of Blood

Blood is a bright red fluid slightly heavier than water, average specific gravity 1.060, and faintly alkaline (pH 7.35). In the arteries it has a scarlet cast and in the veins a purplish hue. Approximately 1/10 of the body weight is blood, some variations occurring in pathological conditions. For instance, an increase in volume (plethora) is associated with polycythemia (pol'e-si-the'me-ah), chlorosis (klo-ro'sis), and in some cases of anemia, but a decrease occurs in infantile diarrhea, absence of drinking water, fevers, severe burns, shock, intestinal obstruction, and in the inhalation of poisonous gases.

## Functions of Blood:

Blood acts to a large extent as the transportation system of the body and its five chief functions are

- 1 To transport nutrients and oxygen to the cells
- 2 To carry waste products from the cells to the organs of excretion

- 3 To transport the internal secretions (hormones)
- 4 To distribute heat and regulate body temperature
- 5 To aid in defending the body against invading disease germs

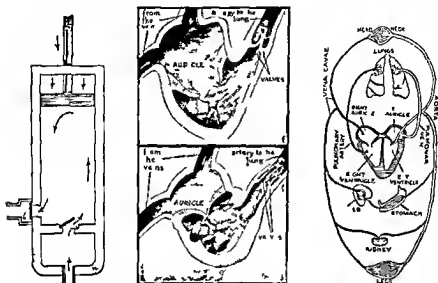


Fig 1—The Human Heart and Blood Circulation. How does the heart operate much like a mechanical pump? Note The term atrium has succeeded the term auricle. Courtesy of New Wonder World.

### Composition of Blood

The composition of blood varies somewhat, but it contains approximately the following constituents

Blood	{	Water 78%		
	{	Solids 22%	Proteins	18.5%
			Glucose	0.1
			Lipids (fats)	1.4
			Salts (inorganic)	1.5
			Waste products etc	0.5

Whole blood consists of a liquid portion called the *plasma* in which are suspended cells or "formed elements" known as the *erythrocytes*, or red corpuscles, the *leukocytes*, or the white corpuscles, and the platelets. The *plasma*, then, is the blood minus the formed elements. In the clotting of blood a soluble protein, called

fibrinogen, changes into the insoluble protein, fibrin, in which are enmeshed the corpuscles. Upon contraction of the blood clot, a clear, slightly yellowish liquid, the serum, separates. Serum then is essentially plasma minus fibrinogen. The following table shows most of the constituents in blood.

CONSTITUENTS IN BLOOD			
Blood	Cells	{ Red blood cells (Erythrocytes) White blood cells (Leukocytes) Platelets	
		Water	
		{ Oxygen Gases { Carbon dioxide Nitrogen	
	Foods	{ Carbohydrate (Glucose) Fat (neutral fat and fatty acids) Protein (amino acids)	
		{ Serum albumin Blood proteins { Serum globulin Fibrinogen	
		{ Chlorides Salts { Bicarbonates Sulfates Phosphates	
	Plasma	—of— { Sodium Calcium Potassium Magnesium	
		{ Urea Nitrogenous waste products { Uric acid Creatine Creatinine	
		{ Antitoxins Protective substances { Opsonins Agglutinins Bacteriolytics	
		{ Hormones (internal secretions from ductless glands)	

### SELF-TESTING QUESTIONS

1. What are the chief functions of the blood?
2. What are the colors of arterial and venous blood?
3. What proportion of the body weight is blood? How does blood react to indicators?
4. State five important constituents of the blood.
5. What is the distinction between whole blood, plasma, and serum?

## II. FORMED ELEMENTS

Suspended in the plasma are three types of formed substances or cells which make up slightly less than one-half the volume of human blood *erythrocytes*, the oxygen carrying cells, *leukocytes*, the disease resisting cells, *platelets*, indispensable for the blood clotting. These cellular substances (corpuscles) may be separated from the plasma by sedimentation, or by centrifuging, and since the corpuscles differ in their density, the major portion of the red corpuscles which are heavier will occupy a layer below the white corpuscles, which have a lower specific gravity.

### Erythrocytes or Red Cells

The red corpuscles normally number approximately 5,000,000 per cubic millimeter in men and slightly less in women. This number may vary greatly under different conditions, such as altitude, exercise, starvation, drug administration, disease, etc. Under the microscope, the red cells appear as circular biconcave discs, whose form changes somewhat in the small capillaries (Fig 2). They have no nucleus, except when found in the bone marrow in the formative stage. The span of life of the red cells is rather short, and a significant number are destroyed daily. Some chemical change apparently takes place rendering them less resistant to destruction, until at the end of from 60 to 120 days they wear out and are destroyed by the reticulo endothelial system which is made up of phagocytic cells in the spleen, liver, and bone marrow. This indicates the necessity for repeated blood transfusions in some pathological conditions in which the normal formation of new red blood cells by the bone marrow is decreased, resulting in severe anemia.

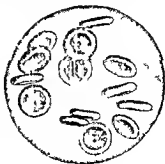
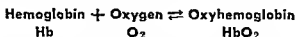


Fig 2—The Gas Carriers Human red cells under the microscope possess a pale greenish yellow color. Courtesy Book of Knowledge by permission of the Grolier Society.

The principal characteristic of the red cells is the red coloring matter, hemoglobin, which is a combination of the protein, globin, and an iron compound, called *hematin*. The main function of the hemoglobin is to combine with the oxygen in the lungs and release part of it again to the tissues.



During respiration, atmospheric oxygen in the lungs diffuses through the walls of the alveoli, and combines with the hemoglobin to form *oxyhemoglobin* ( $\text{HbO}_2$ ), the bright red (scarlet) substance in arterial blood. As the blood circulates through the capillaries in the various tissues, the oxyhemoglobin gives up its oxygen which is used by the tissues for oxidation. Upon this loss of oxygen by the oxyhemoglobin, the resulting hemoglobin imparts a dark red color to the blood, and when seen through the skin has a purplish cast (venous blood). Simultaneously, in the tissue capillaries, excretory products are taken up, chiefly carbon dioxide, which exists mostly as carbonic acid and sodium bicarbonate, a small amount only being combined with the blood proteins. The venous blood combines with this carbonic acid and thus carries the carbon dioxide to the lungs where it is exchanged for oxygen. This cycle is constantly going on and represents the basic process of respiration.

The preceding chemical transformations which occur during respiration are of very great importance, and are more complicated than the above statements indicate. It is the supply of oxygen that makes possible tissue oxidations which are the source of all energy needed by the body, not only for heat formation, but also for the building up and functioning of the tissues. This is especially noticeable in the brain cells where lack of oxygen causes giddiness and fainting spells. A total absence of oxygen, of course, quickly results in death.

The number of red cells varies under different conditions, and the hemoglobin content of each cell may also vary. Blood which contains an increased number of red cells (polycythemia) may impart a brick red color to the skin. On the other hand, a reduced number of these cells (anemia) gives a sallow and bloodless appearance to the skin. This latter condition may result from (1) hemorrhage; (2) failure by the body to manufacture blood; (3) ex-

cessive destruction of red corpuscles by toxins—poisons resulting from chronic suppurating sores or malignant growths or parasites, such as malaria in the blood and certain intestinal worms. With the exception of pernicious anemia, most anemias are treated by dietary measures. It has been shown that pernicious anemia may be controlled by the consumption of certain organ extracts, especially liver extract. These extracts of liver and stomach contain some substance that acts on the bone marrow to form red cells and effective control of pernicious anemia can be accomplished by the injection of liver extract. On this basis pernicious anemia is a deficiency disease. The lack of hydrochloric acid in the stomach of those having pernicious anemia suggests that this disease may be caused by some disturbance in gastric digestion. Two of the B complex vitamins, folic acid (*Lactobacillus casei* factor) and vitamin B<sub>12</sub>, are effective in the control of pernicious anemia. Vitamin B<sub>12</sub> is the active principle in liver extract.

Before leaving the discussion of the red cells we must not forget the fact that they undergo hemolysis (p 103) when diluted with water or treated with a variety of substances (fatty acids, bile acids, snake venom, ether, chloroform, soap, etc.). In some cases, the hemolytic change is so slight that the distended membrane does not burst, but nevertheless allows for the passage of the hemoglobin from the red corpuscles into the plasma.

### Leukocytes or White Cells.

The white cells, of which there are several forms, number about 6000 to 8000 per cubic millimeter. They are larger than the red cells and have a nucleus. Blood which contains an extremely large number of white cells may appear creamy, this pathological condition is known as *leukemia*. Bacterial infection may produce a significant increase in the number of white cells. White blood cell counts are used to assist the physician in detecting infection. The white cells are capable of amoeboid movement, and consequently may leave the blood and enter the tissues. Injury to the cells or infection resulting from bacteria, immediately causes a migration of leukocytes to the infected part where they engulf irritating particles, ingest and destroy the bacteria and degradation products of diseased tissues and cells. This power of white blood cells to destroy bacteria is partly due to enzymes which they contain. Because these white cells take up debris and bacteria, they are often referred to as "the scavengers of the body." Scavenger cells

or phagocytic cells also are present in most tissues. When the tissue cells are injured or infected by bacteria, the condition that results is known as inflammation. The first evidence of inflammation is a dilation of the blood vessels, a slowing of the blood stream. Then the leukocytes migrate to the irritated or infected portion and engulf the irritating particles or the bacteria. In some cases of infection, the number of bacteria is so large that many white blood cells are destroyed by the bacterial toxins with the result that their dead bodies comprise a large part of the *pus* formed.

White cells are produced in lymph nodes, in bone marrow, and in the spleen. In all cases of inflammation, the red appearance of the part involved indicates the presence of a large number of red blood cells, the swelling points to the presence of an excessive amount of blood and lymph, the heat shows that blood has been brought from the deeper structures of the body, and the accompanying pain indicates the pressure of the inflamed tissue and the effect of toxins upon the nerves.

### Platelets:

The platelets numbering about 300 000 per cubic millimeter are smaller than either the red or white cells, and appear as round or ovoid colorless discs. They are not true cells, and little is known about them, but their origin is believed to be in the bone marrow. Upon injury to the blood vessel wall, interference with circulation, or loss of blood, the number of platelets in the blood increases, a fact which suggests that they may, perhaps, have some relation to the white cells. The main function of the platelets is to assist in the changing of soluble fibrinogen to insoluble fibrin in the clotting of blood.

### Clotting of Blood

To prevent loss of blood from the body through mechanical injury to the blood vessels, the blood itself has a way of changing from a fluid into a jellylike solid on contact with injured tissue. According to one theory, blood contains *prothrombin*, which in the presence of calcium ions forms *thrombin*. The thrombin, in turn, changes the soluble fibrinogen (protein) into insoluble *fibrin*.

According to most authorities the mechanism is also dependent upon an activating substance yielded by the platelets, and the platelets are active only when injured. As the fibrin separates from

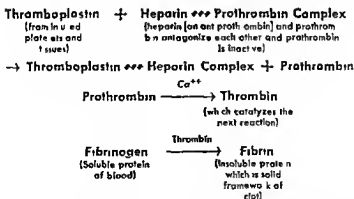


the blood into a network of delicate threads, it holds the formed elements, chiefly red cells, within its meshes to form a jellylike solid called the blood clot. If the clotted blood stands, contraction of the fibrin fibers takes place and causes a pale yellow liquid known as blood serum to separate. Such shrinkage exhibited by fibrin and other colloidal gels is known as *syneresis* (p 113).

The relation between whole blood and serum is as follows: Whole blood minus the formed elements is plasma, plasma minus fibrinogen is serum.

Circulating blood contains platelets, yet coagulation does not occur in the blood vessels. With the knowledge that blood contains prothrombin, calcium ions, and fibrinogen, the question might be rightfully asked why the blood does not ordinarily clot in the blood vessels. This is due to antiprothrombin which inactivates the prothrombin. When blood exudes from the body, the platelets rapidly disintegrate and there is present a substance which neutralizes the antiprothrombin, with the result that the prothrombin, found only in the presence of vitamin K (p 599), is free to act and a blood clot is formed. Strong evidence has been adduced to show this substance is *thromboplastin*, or a closely related substance liberated from the damaged tissues or blood platelets. The thromboplastin counteracts an antiprothrombin, *heparin*, which prevents the change of prothrombin into thrombin.

Summarizing this theory (Howell's) of the normal clotting of the blood may be schematically represented as follows:



The prevention of the clotting of shed blood may be brought about by the removal of the calcium ions ( $\text{Ca}^{++}$ ), one of the essential factors in coagulation. The usual laboratory anticoagulants

are ammonium oxalate and sodium citrate. In collecting blood for transfusions citrate is used since it is nontoxic and can readily be metabolized by the recipient whereas oxalate is relatively toxic when administered intravenously. Commercial anticoagulants are *hirudin*, an extract from leeches, and *heparin*, an extract from liver or lungs. When freshly drawn blood is whipped, the fibrin collects on the apparatus used, leaving a suspension known as defibrinated blood, which will not clot. Usually the clotting time of blood is about three minutes but there are cases of people whose blood is very slow in clotting. These people are called hemophiliacs (bleeders). This condition is hereditary and transmitted only through the female but manifests itself only in the male progeny. Extensive investigations have been made in an effort to determine the nature of the clotting defect in hemophilia but at the present time the cause is not apparent. It may be due to a lack of thromboplastic factors.

Not infrequently, blood clots called *thrombi* occur in blood vessels, the clotting being due mainly to damage of the endothelial lining of the blood vessels. Such clots may cause serious disorders and even death.

### SELF-TESTING QUESTIONS

- 6 What is the chief function of each formed element?
- 7 How are the corpuscles separated from the plasma and identified?
- 8 Why are repeated blood transfusions necessary in some pathological conditions?
- 9 Describe the mechanism by which oxygen and carbon dioxide are carried in the blood.
- 10 Name three conditions producing anemia.
- 11 What produces hemolytic changes in the red cells?
- 12 How do leukocytes differ from erythrocytes?
- 13 How do the white cells function?
- 14 What is pus largely composed of?
- 15 What is the main function of the platelets?
- 16 What is cyneresis?
- 17 What is the explanation for the fact that blood does not ordinarily clot in blood vessels?
- 18 Prevention of the clotting of blood to be used for clinical purposes depends upon what?
- 19 What is used to prevent blood clotting during collection of blood for transfusions?
- 20 What are thrombi and how may they be formed?

### III. ACID BASE BALANCE OF THE BLOOD

#### Constancy of Blood Reaction:

It has been shown how *certain salts in the blood assist in maintaining a constant normal alkaline reaction by counteracting the influence of varying quantities of acids and bases derived from foods*. However, no explanation has been previously given as to how the proteins also function in this respect. Before considering the action of the proteins, it is advisable to turn to page 186 and review the data given on this regulating system of the blood whereby it can take up tremendous amounts of acids and some bases without any appreciable change in its normal alkalinity (pH 7.4). The maintenance of this constant reaction depends mostly upon the amount of available basic bicarbonate ( $\text{NaHCO}_3$ ), the basic and acid phosphates, and the proteins. The functional action of the lungs in eliminating carbonic acid, and that of the kidneys in excreting ammonium salts, or positive ions ( $\text{Na}$ ,  $\text{K}$ ,  $\text{Ca}$ ,  $\text{Mg}$ ) and anions ( $\text{Cl}$ ,  $\text{HCO}_3$ ,  $\text{HPO}_4$ ,  $\text{H}_2\text{PO}_4$ , etc.) are also of great assistance in maintaining this *acid base balance*.

#### Hydrogen Ion Concentration, pH

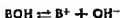
Since the acid base balance of the blood and the hydrogen ion concentration of other solutions are frequently described in terms of pH, it is necessary before proceeding with the study of the blood to refer to page 163 for a general discussion of the significance of this term. For those interested, the accompanying note gives a brief mathematical explanation.

In solution any acid, HA, will dissociate into a varying amount of ions,



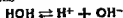
the concentration of the  $\text{H}^+$  ions determining the strength of the acid

A base BOH will likewise ionize to a varying degree in solution,



the strength of the base depending upon the concentration of the  $\text{OH}^-$  ions

When water dissociates



the concentration of the ions is slight. In water, or any aqueous solution, the concentrations of these ions are mathematically related as follows



The  $K_w$  is a constant and by calculation is  $10^{-14}$  at ordinary temperature. Obviously an increase of the  $H^+$  causes a decrease in  $OH^-$ , and *vice versa*. Since a water molecule yields one  $H^+$  and one  $OH^-$ , the concentration for either becomes  $10^{-7}$ , which means that one liter of  $H_2O$  contains  $1/10,000,000$  or  $1 \times 10^{-7}$  gram ions of  $H^+$ . One gram ion of  $H^+$  then is in every 10,000,000 liters of water. In blood there are  $3.98/100,000,000$  or  $3.98 \times 10^{-8}$  gram ions of  $H^+$  per liter. To express very small hydrogen ion concentrations without the use of decimals, Sorensen introduced the

symbol  $pH$  for logarithm  $\frac{1}{H^+}$ . Then in the case of blood,

$$pH = \log \frac{1}{3.98 \times 10^{-8}} = \log \frac{10^8}{3.98} = 7.4$$

the  $pH$  value is the negative logarithm of the hydrogen ion concentration of the solution, expressed in gram ions for each liter.

It should be pointed out again that as the  $pH$  increases the hydrogen ion concentration decreases, and, furthermore, that a change of one  $pH$  unit means a tenfold change in the hydrogen ion concentration. Thus  $pH$  1.0 is ten times as acid as  $pH$  2.0 or 100 times as acid as  $pH$  3.0. Neutrality is  $pH$  7.0 at  $20^\circ$ .

pH	Hydrogen Ion Concentration in Gram ions per Liter	
14	$10^{-14}$	Increasing Alkalinity
13	$10^{-13}$	
12	$10^{-12}$	
11	$10^{-11}$	
10	$10^{-10}$	
9	$10^{-9}$	Neutral
8	$10^{-8}$	
7	$10^{-7}$	
6	$10^{-6}$	Increasing Acidity
5	$10^{-5}$	
4	$10^{-4}$	
3	$10^{-3}$	
2	$10^{-2}$	
1	$10^{-1}$	
0	$10^0 = 1$	

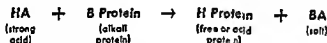
### Proteins as Buffers.

With the understanding that proteins contain basic groups,  $-\text{NH}_2$ , and acid carboxyl groups,  $-\text{COOH}$ , we can understand how the blood proteins, including hemoglobin (Hb) and oxyhemoglobin ( $\text{HbO}_2$ ), can act as buffer substances in regulating the acid base balance by preventing changes in hydrogen ion concentration when small amounts of acids or bases are added. In the case of the proteins there are three possible ratios

$$\frac{\text{HHbO}_2 \text{ (free oxyhemoglobin)}}{\text{BHbO}_2 \text{ (alkali salt of oxyhemoglobin)}} \quad \frac{\text{HHb (free or acid hemoglobin)}}{\text{BHb (basic hemoglobin salt)}}$$

$$\frac{\text{H protein (free protein)}}{\text{B protein (alkali proteinate)}}$$

The action of protein in neutralizing an acid is as follows



Whereas the strong acid dissociates to give large numbers of hydrogen ions, the acid protein dissociates but slightly to give relatively few hydrogen ions

### SELF-TESTING QUESTIONS

- 21 What are buffers?
- 22 Using the carbonate or phosphate buffer mixture explain how the blood remains normal upon the addition of acids and bases resulting from metabolic changes
- 23 Why can proteins act as buffers?
- 24 What two kinds of acting substances make up all buffer pairs? (p 187)

From the discussion on pages 185 to 187 and herein, it is evident that there are five lines of defense to resist change in the hydrogen ion concentration, and of these the buffer effect proper of bicarbonate in the blood is relatively unimportant compared with that of the hemoglobin

#### IV. BLOOD CHEMISTRY

##### Tests for Blood

Quite frequently occasions arise when there is a demand for knowing whether a stain is blood, and if so whether it is human blood. Of the chemical tests to determine the presence of blood, the *hemin test* is very satisfactory. The technic involves boiling the stain in question with glacial acetic acid and sodium chloride, cooling and making microscopic examination for crystals of hemin or bismuth chloride. Another test for blood which is very sensitive and is used for the detection of blood in biological material such as urine, feces and gastric juice is the *benzidine test*. In this test a solution of benzidine in glacial acetic acid is mixed with hydrogen peroxide and the material suspected of containing blood. In the presence of blood an intense blue color develops. Dilutions of blood as great as 1 to 500,000 can be identified by this method.

It is only within recent years that a method has been developed to make an absolute differentiation of human blood. This is a biological test based upon the fact that the blood serum of any animal which was previously injected only with human blood produces a precipitate only with human blood. Such a test is good for stains that have dried even for months and will show positive results in dilutions as high as 1 to 50,000.

##### Blood Groups and Transfusion

For a long time, it has been known that the blood serum of some people will agglutinate (clump) or hemolyze blood cells of other people, and that this is the main cause of severe reactions that may follow blood transfusions. Investigation has shown that the red cells of a given individual may contain either one or both of two agglutinable substances A and B, and that the serum from a given individual may contain either or both of two isoagglutinins or antibodies, anti A and anti B. The reactions of different cells and sera show the presence of four blood groups, namely O, A, B, and AB. Thus there are four types of cells as follows: 1 Those that contain agglutigen substance A, 2 Those that contain agglutigen substance B, 3 Those that contain both A and B, and 4 Those that contain neither agglutigen substance A or B. Correspondingly the serum may contain antibodies or isoagglutinogens in four combinations: 1 An antibody for A, 2 An antibody for B, 3 Antibodies for both A and B, and 4 No antibodies for either A or B.

Since, in addition to the nomenclature by letters, the numberings are still in use, their relationship is presented as follows

<i>Nomenclature by Landsteiner</i>	<i>Jonsky</i>	<i>Moss</i>
O	I	IV
A	II	II
B	III	III
AB	IV	I

In blood typing the problem is to find the type of the donor's blood and the type of the recipient's blood. After a donor of the proper type is obtained for a recipient, a compatibility test is usually carried out in which donor's and recipient's blood are mixed. The discovery of the blood groups in man has cleared up many untoward effects observed prior to this knowledge.

The table on page 455 shows the types of reactions.

Notice that *no agglutination takes place when the blood cells of the donor and the serum of the recipient belong to the same group*.

### The Rh Factor in Blood

In addition to the four major blood groupings—types A, B, AB and O, which make safe transfusions possible, there also are other factors or agglutinable substances (antigens) for which ordinarily no corresponding isoagglutinins (antibodies) are found in human sera. It is these antigens which, without corresponding antibodies, may present medical problems in human transfusions.

Prior to World War II it was known that the blood of a mother could cause the death of her own baby even though both parents belonged to the same blood group. In 1940 it was discovered that the blood of the rhesus monkey injected into a rabbit produced an antibody (agglutinin) in the serum, which clumped not only the red cells of the monkey, but also the red cells of about 85 per cent of white people notwithstanding their major blood group.

This agglutinable substance is called the Rb factor.

Rhesus monkey

















or Rh+ blood (injected into) rabbit = antibody formation

This rabbit serum

mixed with human blood = / agglutination in 85% (Rh+)

\ no agglutination in 15% (Rh-)

## METHOD OF TESTING BLOOD GROUPS

Recipient— Serum of Group			Donor—Red Blood Cells of Group				Remarks pertaining to the vertical columns O, A, B, AB
Inter- national	Jan- sky	Moss	O	A	B	AB	
O	I	IV					Cells of Group O not agglutinated by any sera. Contain no agglutinable substances. Universal Donors (45 per cent of adults)
A	II	II					Cells of Group A agglutinated by sera of Groups O and B (40 per cent of adults)
B	III	III					Cells of Group B agglutinated by sera of Groups O and A (ten per cent of adults)
AB	IV	I					Cells of Group AB agglutinated by sera of Groups O, A, B. Serum of Group AB contains no isogglutinins. Universal recipient (5 per cent of adults)

When recipient is group O, select donor from group O

"	"	"	"	A <sub>c</sub>	"	"	"	"	O or A
"	"	"	"	B <sub>c</sub>	"	"	"	"	O or B
"	"	"	"	AB <sub>c</sub>	"	"	"	"	O, A, B, AB

If possible use donors of the same group and not universal donors

Why is group O called the universal donor, and group AB a universal recipient?

The 85 per cent are termed Rh positive (Rh+), and the remaining 15 per cent are Rh— (Fig 4).

And here is where the trouble starts

When Rh+ blood gets into the blood stream of an Rh— person the tissues combat Rh+ by making antibodies (agglutinins) which





Fig 3—Testing for Rh The small vial (left) contains enough serum to make hundreds of tests to find out whether blood is Rh positive After the blood to be tested has been diluted with salt solution, it is put in the tube with the anti Rh serum (right) Courtesy Science Service

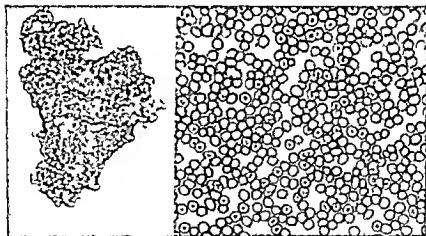


Fig 4—Final Blood Examination After incubation and centrifuging, the blood is examined under a microscope If the cells have clumped together (left), then the blood is positive Rh blood If the cells show distribution after the blood is put in the tube with the anti Rh serum, then the blood is Rh negative (right) Courtesy, Science Service

in repeated transfusions destroy Rh+ red cells, and the patient becomes violently ill and may die, primarily as a result of kidney damage by the destroyed red blood cells (Fig 4)

In pregnancy when the mother is Rh- and her baby Rh+ (inherited from Rh+ father), blood from the unborn travels into the mother's blood stream to produce antibodies, some of which return

to the child and destroy blood cells. Miscarriage, stillborn, death soon after birth, erythroblastosis (a hemolytic disease), and in some instances feeble-mindedness may occur. No harm results however, if an Rh- mother has an Rh- child. In modern hospitals stocks of Rh- blood from professional blood donors are kept ready to administer to a newborn baby. The plasma is always safe since it contains no red cells and hence no Rh factors.

From this brief discussion it is evident that blood should be typed for Rh factor as well as for the major blood group types. It is important to avoid giving an Rh- recipient Rh+ blood and is also important in anticipating problems arising from an Rh- mother having an Rh+ baby.

### Collection and Preservation of Blood

In a physiological sense the blood must reflect the condition of every tissue and any disease or change involving the fixed tissues of the body. Studies have shown that in some instances these changes are so characteristic of certain diseases that they may be regarded as constant signs and often the most important part of the clinical picture, and diagnosis is impossible without a knowledge of them. Knowledge of these blood changes, therefore, is necessary for diagnosis, prognosis, and treatment of many of the internal diseases encountered by practicing physicians. In some, the blood changes alone are sufficiently characteristic to establish the diagnosis, but more often they are only suggestive, and must be interpreted in the light of all additional clinical evidence that may be obtained.

Compared to a few years ago, when blood tests were quite difficult, we now find that some blood tests are simple, rapid and accurate enough to be carried out in the physician's office.

In hospital work, chemical blood analyses are now made so frequently and in such large numbers that the nurse must know how to take and preserve blood specimens.

If possible, the blood should be collected in the morning, before any food or liquid has been taken. The blood is more uniform at this time and permits an analysis to be made on the same day instead of standing over night and undergoing some changes.

If the blood is immediately refrigerated, it may be kept for a few hours but the sooner the test is made the more satisfactory are the results. The nurse may be asked to assume responsibility for immediate delivery of the sample to the laboratory.

The amount of blood required for chemical studies may vary from a fraction of a milliliter which can be collected from a finger tip or ear lobe to 10 to 20 ml of blood which is collected from a vein. If a glass syringe is used the blood should immediately be discharged into a one ounce bottle which contains two drops of a 20 per cent solution of potassium oxalate, this latter substance acting as an anticoagulant. The contents of the bottle should be mixed (not shaken) with a rotary motion to allow mixing with the oxalate solution.



Fig 5— $\text{CO}_2$  Combining Power of Blood. Carbon dioxide is carried from the tissues and to the lungs chiefly in combination with fixed bases which are important buffer substances in the blood. When the alkali reserve is diminished the carbon dioxide carrying capacity of blood is correspondingly decreased. The picture below shows the van Slyke method of determining the carbon dioxide combining power of blood. When the alkali reserve is decreased beyond a certain point what condition may be said to be present? Courtesy Parke Davis & Co.

When the blood is to be employed for acid base balance studies i. e., pH and CO<sub>2</sub> determination) (Fig. 5) it should be drawn with minimal stasis. This may be done with or without the use of a tourniquet. However, when the needle has entered the vein, and a tourniquet has been used, it should be released and a minute's time should elapse before blood is drawn. Furthermore, the blood must be drawn and preserved under mineral oil, which protects the specimen from the CO<sub>2</sub> of the atmosphere. When extreme accuracy is not of vital importance, CO<sub>2</sub> determinations may be made on blood which was not protected by a layer of mineral oil, if the analysis is promptly carried out.

### **Blood Analysis as an Aid in Diagnosis and Prognosis:**

In addition to the importance of being able to take and preserve blood specimens, a nurse should be able to interpret the figures resulting from laboratory tests. For instance, N. P. N. 50 should have a meaning and give some indication of a patient's condition. With that in mind the table on page 460 is inserted to show the range of changes usually encountered in several common metabolic disorders.

Notice the numbers indicating the normal and the pathological change, and also the significance attached to abnormal amounts of the different blood constituents.

Of particular interest and importance in the table are the readings in nephritis. Normally the kidney eliminates the nonprotein nitrogen (N. P. N.) waste products (urea, uric acid, and creatinine), and is impenetrable to colloidal materials (proteins); but when damaged the permeability changes, and the extent of the retention of the waste products is often an index of the severity and progress of the disease. Such readings are a helpful guide to the physician.

Another disease of not uncommon occurrence is diabetes, believed to be occasioned by damage to pancreatic cells, which fail to secrete sufficient insulin for proper metabolism of sugar. Notice the low and high readings for sugar (40 to 1300) and the low and high readings for carbon dioxide capacity (5 to 130), the low reading indicating a reduction of base forming materials (the alkaline reserve of the blood) that is always associated with acidosis (acetone, acetoacetic and beta hydroxybutyric acids). When the acids use up the alkaline reserve (alkali available to combine with CO<sub>2</sub> and other acids) the blood cannot combine with as much carbon dioxide as formerly. Consequently, the determination of the amount of carbon dioxide that can combine with the blood shows how much

## CLINICALLY SIGNIFICANT BLOOD CONSTITUENTS\*

<i>Blood Constituents Tested for per 100 ml of Blood</i>	<i>Normal Range (Units per 100 ml of Blood or Serum)</i>	<i>Begin- ning Patho- logic Range†</i>	<i>Patho- logic Range</i>	<i>Significance</i>
Hemoglobin	14-17 Gm	-12	3-23	Low in anemia High in polycythemia
Total plasma protein	6.0-8.0 Gm	-6.0	3.0-6.0	Low in nephrosis, low in protein deficiency
Plasma albumin	3.6-5.6 Gm	-3.5	1.0-3.6	Low in nephrosis, low in protein deficiency
Plasma globulin	1.3-3.2 Gm	-1.3	0.4-1.3	Low in nephrosis, low in protein deficiency
Nonprotein nitro- gen (N P N)	25-35 mg	+35	20-400	High in nephritis
Urea nitrogen	12-15 mg	+20	5-350	High in nephritis
Creatinine	1-2 mg	+3.5	to 34	High in nephritis
Uric acid	1-3.5 mg	+4	to 27	High in nephritis, gout
Blood sugar	70-120 mg	+150	40-1300	High in diabetes
CO <sub>2</sub> capacity	50-70% by volume	-45	5-130	Low in nephritis, aci- dosis high in alkalosis
Cholesterol	140-170 mg	-130 +170	60-1000	High in nephritis low in anemia
Serum calcium as calcium	9-11 mg	-8	3-20	Low in tetany, stages of nephritis high in hyperparathyroidism
Serum inorganic phosphorus as phosphorus				Low in rickets High in stages of nephritis
Adult	2.5-4 mg		2-4	
Children	4-6 mg	-4		
Chlorides as NaCl				High in nephritis with edema, nephritis, eclampsia, low in pneumonia
Plasma	570-620 mg	-500	300-850	
Whole blood	450-520 mg	-450	120-700	
Icterus index (terms of 1:10,000 potas- sium dichromate)	4-6	+10	10-225	High in hemolytic ane- mia, hepatic jaundice, and obstructive jaun- dice Indicates liver disturbances

\* Myers V C J A M A vol 91

† Below is indicated by a (-) sign and above by a (+) sign.

of the alkaline reserve has been used up in neutralizing these acids and it will represent the extent of acidosis

Normally, the blood contains about 0.1 per cent (70 to 120 mg per 100 ml) of blood sugar, which may increase to about 0.2 per cent before the kidneys become permeable and allow it to pass into the urine. In diabetes the concentration runs even higher. The blood sugar test is valuable not only in diagnosing diabetes and in treating the disease after glucose or insulin injections but also in determining the blood sugar tolerance in endocrine (thyroid and pituitary gland) disturbances.

Finally, one more disease will have to be mentioned among those in which blood analysis aids diagnosis, a disease called anemia, in which the hemoglobin is considerably lower than normal content of 14 to 17 Gm of hemoglobin per 100 ml of blood. This may be the result of a reduced number of red cells or a reduced amount of hemoglobin in the cells which may result from hemorrhage or in infectious diseases such as diphtheria and syphilis. With a low hemoglobin content, the oxygen carrying capacity of the cells is so small that partial tissue asphyxia may result. Diets for anemia patients must be nutritious and contain sufficient iron and protein for the production of hemoglobin. Recent experiments indicate that copper in foods in some way—probably as a catalyst—stimulates the utilization of iron in the formation of hemoglobin.

From the preceding brief discussion, it is evident that blood analysis gives first hand information concerning many diseases, and in many cases more definite information than urinalysis. In the case of diabetes in particular, a blood sugar analysis may indicate the presence of the disease long before such an indication could be found by analysis for sugar in the urine.

As a remaining statement, blood analysis has also given helpful information in diagnosis and prognosis of such diseases as gout, nephrosis, mercury poisoning, urologic conditions, eclampsia, intestinal obstruction, alkalosis, certain malignant conditions, tetany and rickets.

### SELF-TESTING QUESTIONS

- 25 What is a test for blood?
- 26 How can human blood be differentiated from other bloods?
- 27 What is the basis of blood grouping?
- 28 What is meant by the Rh factor?
- 29 Abnormal amounts of what substances in the blood indicate kidney disturbances?
- 30 What does a high N P N indicate?

- 31 In diabetes what blood constituents would have a high or low reading?  
 32 Why is the blood sugar test important?  
 33 What kind of blood determination is used in anemia?

## V. PLASMA

### Function of Plasma

The plasma, a faint yellowish liquid, makes up slightly over one half of the volume of whole blood, and contains solid matter dissolved or in colloidal condition. It is this colloidal nature of plasma which makes it viscous and somewhat translucent. The approximate composition of plasma is shown in the table below.

Plasma usually is regarded merely as a vehicle for transportation of erythrocytes. Obviously, its true significance is not always recognized. What the erythrocyte is to gaseous ( $O_2$ ,  $CO_2$ ) metabolism, the plasma is to nitrogen, mineral, and water metabolism. The plasma supplies the fuel, and the erythrocytes supply the oxygen needed for internal combustion. In a sense, the plasma itself constitutes a liquid fuel. It distributes food glucose, amino acids and lipids. It is the medium for chemical reactions, it transports enzymes, hormones and specific products of cells to their allotted

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Plasma (sp gr 1.025)	Water	91%	Proteins (serum albumin, serum globulin and fibrinogen) 70% Salts (inorganic) 10% Fat sugar and other organic substances 10%
	Solid	9%	

---

seat of action, it removes and conducts waste products to the organs of excretion, it carries the materials necessary for repair, it automatically and immediately seals ruptured walls of the blood vessels, and it regulates heat. The plasma, therefore, is a marvelous internal medium which in health is continuously replenished and purified, and yet is maintained at a remarkably constant volume and composition.

### Function of the Plasma Proteins

Of the solid matter in the plasma, the larger part is protein, namely, serum albumin, serum globulin, and fibrinogen. Together with the lipids (fat like substances), these proteins form the structure of the plasma.

The fact that blood contains a great amount of water (78 per cent) and therefore is more fluid than other tissues is due primarily

to the characteristic property of the colloids (proteins) in absorbing and holding the water in the form of gel. As has been mentioned (p 186) and is more fully discussed on page 452, the proteins, as well as certain salts, act as buffers in regulating the normal reaction of the blood.

As an additional function, the plasma proteins assist in the elimination of waste products in the cells. There are other functions of the plasma proteins, the most important of which is to maintain normal osmotic pressure between the blood and tissues. In the state of shock, when plasma proteins leave the vascular bed, the blood is left in a concentrated condition. Administration of albumin or blood plasma is valuable in relieving this condition. Furthermore, we must not forget the special function of soluble fibrinogen in changing into insoluble fibrin to form the blood clot (p 447).

#### Other Plasma Constituents

The small amount of inorganic salts present in the plasma are mostly sodium chloride and bicarbonate. In still smaller amounts are found potassium, calcium, and magnesium salts. Reference (p 188) has already been made to their chief physiological uses, their special properties, and their importance in health and life.

The fats and lipids, lecithin and cholesterol are studied under the various functions of the blood.

#### SELF-TESTING QUESTIONS

- 34 What is the main function performed by the plasma?
- 35 What other functions are attributed to the plasma?
- 36 What is the role of the plasma proteins?
- 37 The plasma proteins give what properties to the blood?

### VI. FUNCTIONS OF THE BLOOD

#### Transportation of Nutrients and Oxygen:

As stated, one important function of blood is to transport nutrients in solution from the intestines and storage depots, and oxygen in combination with the hemoglobin of the red cells from the lungs to the tissues. As a result of the digestion of general foodstuffs containing carbohydrates, fats, and proteins, we find glucose, resynthesized fats, amino acids, inorganic salts, vitamins, and water in the blood. These materials, along with the oxygen from the lungs, are carried by the blood to the cells where they may be used either as fuel for the conversion of chemical energy to me



chemical or heat energy, or to build tissue. Although during absorption of these nutrients, the concentration is greater, still it does not increase very much, because of rapid use or storage by the tissues. This is especially true in the case of high protein consumption, for very little accumulation of amino acids occurs in the blood. The ingestion of large quantities of sweets may run the sugar content of the blood from 0.09 to 0.2 per cent but utilization by the tissues and the conversion into glycogen by the liver and muscles soon reduces it to normal. In case glucose does accumulate in the blood at a faster rate than it can be used or stored by the tissues the threshold point of the kidneys is reached and sugar will be excreted into the urine—a nonpathological condition referred to as *alimentary glycosuria*. The quantity of fats and fatty acids in the blood may increase for a short time following fat ingestion to an even greater extent than glucose, occasionally imparting a milky appearance to the blood.

The water and inorganic salts are absorbed rapidly from the intestines, but excessive dilution of the blood and an abnormal change in the osmotic pressure is prevented by elimination of water and salts through the kidneys.

In certain diseased states it may be desirable to supply nutrients directly to the blood by intravenous administration. It is also desirable in some conditions to supply needed salts or electrolytes. The table on the following page shows some of the more commonly used intravenous solutions.

### Transportation of Waste Products

The second important function of the blood is to transport waste products of metabolism from the tissue cells to the organs of excretion (kidneys, lungs, intestines, skin and liver which eliminates waste products in the bile). The following table shows the important waste products handled by the excretory organs.

#### EXCRETORY ORGANS AND THEIR WASTE PRODUCTS

Kidneys	Lungs	Intestines	Skin	Liver
Water	Water	Water	Water	Water
Salts		Salts	Salts	Salts
N Compounds		N Compounds		N Compounds
Pigments etc	Carbon dioxide	Pigments etc Food residues		Pigments etc

## REPRESENTATIVE SOLUTIONS FOR PARENTERAL USE

<i>Preparation</i>	<i>Vehicle</i>	<i>Also Known As</i>
Saline (NaCl) 0.9%	Distilled Water	Physiological Saline Normal       " Isotonic       "
Ringer's 0.86% NaCl 0.03% KCl 0.033% CaCl <sub>2</sub>	Distilled Water	
Invert Sugar 10%	Distilled Water	Travert <sup>®</sup> *
Dextrose 5% to 20%	Distilled Water	Glucose 5% to 20%
Amino Acids, Peptides and Polypeptides	5% Dextrose, distilled water or saline	
Darrow's Solution 0.27% KCl 0.30% NaCl 0.60% Na lactate	Distilled Water	
Potassium Chloride 0.3%	10% Invert Sugar	
Lactate Ringer's 0.60% NaCl 0.03% KCl 0.02% CaCl <sub>2</sub> 0.31% Na lactate	Distilled Water	Hartmann's
Alcohol 5%	0.9% Saline 5.0% Dextrose	

Whole blood and plasma are also commonly used, as well as the commercially obtainable plasma,—albumin and globulin \*<sup>®</sup> means registered name

The inorganic salts include the bicarbonates, chlorides, phosphates, and sulfates. The nitrogenous substances usually referred to as the nonprotein nitrogen (N. P. N.) are creatinine, urea, uric acid, and ammonium compounds.

Since all absorbed foods (glucose, fats, amino acids) contain carbon, hydrogen and oxygen, the two main products of oxidation are carbon dioxide and water. In the case of amino acids we have

certain nitrogenous substances (mostly urea) also formed, while if sulfur and phosphorus are present they are oxidized to the corresponding sulfates and phosphates. The chlorides undergo no change. The carbon dioxide as has previously been stated unites with water, with the alkali or proteins present, or dissolves in the blood, and is carried to the organs of excretion.

### Transportation of Hormones.

A third important function of the blood is to transport for distribution and utilization secretions, or *hormones*, of certain glands (endocrine). These glands are often referred to as the ductless glands since their secretion is poured directly into the blood. Hormones stimulate certain tissues, and in this way harmonize the activities of organs located in different parts of the body.

For instance, the blood carries from the ovarian gland a secretion which affects the development of sex characteristics of various parts of the body. In a few instances, however, glands may have both an external secretion and an internal secretion. An example of such a case is the pancreas in which the pancreatic juice is the external secretion and insulin is the internal secretion, insulin being the hormone which has an important role in carbohydrate metabolism. Although the amount of secretion is very small, its influence on metabolism is very great.

### Diffusion of Heat.

This is a fourth function of the blood. In oxidation of foods and of devitalized tissue, or as a result of other metabolic changes in the body, energy is liberated. During rapid oxidation of glycogen or fat in the more active tissues, such as muscles, the blood quickly moderates this localized higher temperature by distributing the heat through the circulating blood to the surface of the body where it is lost by conduction and radiation. Then the blood vessels are dilated, and the skin becomes flushed. Water can store more heat than the same volume of any other substance and as a consequence the water of the blood absorbs heat, and upon evaporation from the sweat glands and mucous surfaces, assists in regulating body temperature. Exposure to cold causes a contraction of the blood vessels and diminishes the cooling area of the surface blood vessels with the consequence that relatively little blood reaches the surface of the body to lose heat. At such times, the skin may appear pale and numbness may even result.

## Defensive Action of the Blood

A fifth important function of the blood is to aid in defending the body against invading disease organisms, a function performed by the white cells and the antibodies. This function has already been discussed (p 446)

## Other Blood Constituents

There are many remaining substances in the blood, but space does not permit a discussion of them. There are, however, two lipids, *lecithin* and *cholesterol*, that deserve mention. These are primary cell constituents that supposedly have some relation to the transportation of fat to the tissues, and the intermediary metabolism of fats. Their determination is of diagnostic value in certain pathological conditions (diabetes, nephritis, anemia, etc.). The blood also contains certain enzymes such as amylase and phosphatase. The measurement of blood amylase concentration is quite useful in the diagnosis of acute pancreatitis since in this condition it is markedly elevated. Phosphatase concentration is increased in certain bone disorders. There are also present antienzymes, which can inhibit enzyme action, and antibodies which can combine with and counteract the effect of toxins elaborated by bacteria.

## Tissue Oxidation

This is a fascinating but rather difficult field of biochemical study. Recent experiments *in vivo* and *in vitro* have thrown much light on the subject but it is rapidly changing. A few general statements must suffice in this course.

The oxidase enzymes present in tissues bring about certain types of oxidation in the presence of certain organic intermediates. There is another mechanism which is known as "dehydrogenation" or loss of hydrogen, which really amounts to oxidation of the substance which loses the hydrogen. An interesting example of this type of reaction is that of glutathione. It has been synthesized and concrete facts about its action are now well known. It is an excellent example of an organic "hydrogen acceptor," that is, it accepts hydrogen from the substance being oxidized and thus becomes reduced itself. It later becomes oxidized again, and functions over and over again as a "hydrogen acceptor," thus favoring tissue oxidations.

## SELF-TESTING QUESTIONS

- 38 What are the most important nutrients carried by the blood?
- 39 What nutrients are present in increased amounts in the blood following the ingestion of large quantities of food?
- 40 What is meant by alimentary glycosuria?
- 41 What are two main waste products of metabolism?
- 42 What happens to most of the nitrogenous foods?
- 43 What salts are most likely to occur in the excreta?
- 44 What is a hormone?
- 45 Explain how the blood helps to equalize body temperature
- 46 How does the blood defend the body against disease?
- 47 What is one function of lecithin? of cholesterol?
- 48 How does oxidase assist in tissue oxidation?

## VII EXTRACELLULAR WATER AND LYMPH

## Functions of Lymph

Since the blood in its circulation to all tissues of the body is in a closed system of blood vessels, a more intimate communication with the individual cells is brought about by another liquid, namely the extracellular body water, a colorless watery fluid surrounding each cell. It is derived from the blood and the tissues by a passive ultrafiltration process, and so closely resembles blood plasma that it is often thought of as "blood without the red corpuscles or protein." It is via the extracellular water that the cells obtain their food and discharge their waste material. The extracellular body water therefore may be considered as the "middle man" or "go-between" for blood and tissues. Not only is it the means by which food materials of the blood diffuse into the cells of all tissues, but it is also the medium through which the products of chemical activity in each cell gain access to the blood. There is a continuous exchange of materials going on between the cells and the blood plasma via the extracellular water. Its composition closely resembles that of the plasma, and whenever fluctuations in the concentrations of the constituents take place, the diffusible substances pass with ease and rapidity between the blood and the tissue cells under normal conditions.

Lymph and extracellular water have an almost identical composition. When extracellular water enters the small blind ended vessels known as the lymphatics it is then usually called lymph. These vessels are distributed among practically all of the body cells. They unite to form larger vessels which eventually pour their contents into the blood stream chiefly through the thoracic

duct This is one of the large lymph vessels It is the general trunk of the whole lymphatic system, draining the smaller lymphatics from the legs, abdominal organs and left side of the body It is about 20 inches long and empties into a large vein of the neck on the left side, at the junction of the subclavian and internal jugular veins Under normal conditions there is a continuous movement of water from the capillary blood vessels to the extracellular spaces and in turn into the lymphatics It is in this way that most of the lymph is returned to the blood again The advantage of the position of the extracellular water between body cells and blood is that it makes the exchange of materials between blood and body cells easier In addition, the lymph, in its circulation through the body, filters through lymph nodes or glands, and in this way it can collect, remove, and destroy much foreign material such as infecting bacteria, which may have entered the tissues This destruction of bacteria often prevents the spread of infection to different parts of the body

### VIII. ANTIBIOTICS AND SULFA DRUGS

The *antibiotics* are organic substances of complex character which are usually produced by microorganisms and are used to combat certain pathogenic bacteria In this category of anti-bacterials penicillin, streptomycin, Aureomycin and Chloromycetin are outstanding

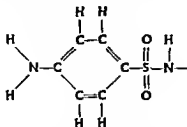
Penicillin, of which there are several types, has been more thoroughly studied than others, it is produced by the fungus or mold called *Penicillin notatum* which is grown commercially on a large scale in a liquid culture medium Penicillin G is quite effective, and in the form of the calcium or sodium salt it is given by intravenous or intramuscular injection, or by surface application in the treatment of numerous infections

Streptomycin, a product of a soil microorganism, is produced today in considerable quantity from cultures As an antibiotic streptomycin is effective against certain pathogenic microorganisms which are impervious to penicillin, and it is used in treating such infections as tuberculosis, tularemia, typhoid fever and wound infections

Chloromycetin is of interest inasmuch as it is the first antibiotic to be successfully synthesized artificially Like streptomycin, this antibiotic is produced in nature by a soil microorganism Chloromycetin has proven effective in treatment of virus pneumonia

The study of antibiotics is today one of the very active fields of biochemical research, and it is quite probable that other useful substances of a similar nature will be found

The *sulfonamide* or "*sulfa*" drugs are synthetic chemicals which have proven valuable in treating various bacterial infections. The sulfonamides are derivatives of sulfanilamide, (p. 321) and all have in common the following unit of structure



Of the many compounds of this type that have been synthesized, four are sufficiently important to warrant mention

Sulfanilamide results when a hydrogen atom is attached to the free bond of the above structure. Sulfapyridine, sulfathiazole and sulfadiazine are formed by attaching a pyridine, thiazole or diazine nucleus respectively to the free bond of the structure pictured. The derivatives of sulfanilamide are less toxic and more effective than sulfanilamide itself. These drugs have value in treating pneumonia, infections of the blood stream, streptococci infections, etc. In some individuals serious reactions develop from the use of sulfa drugs, hence they should never be employed without the direction of a physician.

### SELF-TESTING QUESTIONS

- 49 How does extracellular water differ from blood?
- 50 What is the main function of the lymph?
- 51 What are the advantages of having a separate lymphatic system between the cells and the closed system of blood vessels?

### SUGGESTED ACTIVITIES

#### I. THOUGHT PROVOKING QUESTIONS

- 1 Why is there a need for a circulatory system?
- 2 How does the blood in the right auricle (atrium) differ from that in the pulmonary vein?
- 3 Compare and contrast in tabular form the erythrocytes, the leukocytes and the platelets with regard to their structure, function, and site of formation.

- 4 What dietary precautions should be observed in nephritis in diabetes and in anemia?
- 5 Why could the body not exist without lymph?
- 6 During colds and other infections the lymph nodes frequently swell. Why is this?
- 7 Under what circumstances might it be desirable to know whether a given sample of blood is human blood?
- 8 Does the formation of pus in a wound always indicate an infection?
- 9 Under what varying conditions are blood transfusions necessary?
- 10 Is it ever desirable to let blood out of the body as the early surgeons used to do either by bleeding the patient or by using leeches?
- 11 Why is hemophilia a dangerous disease? What treatment is used?

## II PROJECTS

- 1 Read some *additional material on the chemical analysis of blood*. Study the hospital charts of patients with diabetes and nephritis with special regard to the blood chemical studies.
- 2 Make a list of the various fluids in the body and show in tabular form the composition and chief functions of each.

## III VOCABULARY TESTING OF NEW TERMS

plethora	anemia	fibrin	hormone
plasma	leukemia	agglutination	antienzyme
erythrocytes	prothrombin	hemophilia	antibody
leukocytes	thromboplastin	thrombi	lymph
platelets	heparin	isoagglutinins	serum
dehydrogenation	hydrogen acceptor	glycosuria	thrombin
polycythemia	fibrinogen		

## IV TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Anticoagulants for Blood
- 2 Hemophilia
- 3 Biological Significance of Heme
- 4 Blood Banks and How They Are Maintained
- 5 Theories about Blood Clotting

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 741-744



## URINARY EXCRETION

## CHAPTER OUTLINE

- |   |   |
|---|---|
| <b>I. EXCRETION</b><br>(a) Anatomical and physiological correlation<br>(b) Excretion, products and pathways<br>(c) How the kidneys form urine | (c) Physical examination of urine volume, color, transparency, odor, specific gravity, reaction   |
| <b>II. EXAMINATION OF URINE</b><br>(a) Importance of urinalysis<br>(b) Collection of urine for analysis                                       | <b>III. COMPOSITION OF URINE</b><br>(a) Organic constituents<br>(b) Inorganic salts<br>(c) Abnormal constituents<br>(d) Urinary calculi |

## I. EXCRETION

**Anatomical and Physiological Correlation:**

It is assumed, that before coming to class, the students have reviewed the anatomy and functions of the kidneys, as it is not convenient to do so, except in a very general way, in this discussion. Indeed, the mastery of biochemistry will be greatly aided if a constant attempt is made to correlate other allied subjects with the chemical principles presented in this course. Frequent reference to illustrations in other texts will help one to understand difficult problems presented in the study of chemistry. The very background of biochemistry is the study of those chemical changes in organs (anatomy) and tissues (histology) which take place during active function in health (physiology) or in disease (pathology). Therefore, it is best to try to view the facts of biochemistry in relation to structure and function, rather than as an isolated subject.

**Excretion; Products and Pathways:**

When food is ingested it undergoes a series of hydrolysis reactions and is eventually broken down to simple compounds that include monosaccharides, amino acids, fatty acids, and glycerol. These substances along with minerals and water are absorbed from the intestine into the blood stream and are thus made available for use by all body cells. In general, the cells carry out two types of reactions with these substances; they may be oxidized and broken down to carbon dioxide, water, and simple nitrogen compounds or they may be synthesized into complex substances. The first of the reactions is responsible for the conversion of chemical energy to heat energy and mechanical energy, whereas by synthesis new body

tissue is formed along with specific products which include hormones, enzymes, and a variety of other substances.

As a result of the chemical metabolic reactions, waste products are produced which must be excreted. These include water, carbon dioxide, urea, and other simple nitrogen compounds. In addition to these major waste products the body also has numerous other substances to be excreted which include: ingested water, substances absorbed from the food for which the body has no use, products arising from detoxification reactions, excess minerals, etc.

The pathways of excretion are the kidneys, the lungs, and to a lesser degree, the gastrointestinal tract, the liver and the skin. Most of the carbon dioxide excretion and a considerable portion of water excretion is carried out by the lungs whereas excretion of nitrogenous waste product is almost totally dependent on the kidney. We shall now consider the mechanism by which the kidney functions.

### How the Kidneys Form Urine:

The process by which the kidneys secrete urine is quite complex. Figure 1 is a diagram of the nephron which is the microscopic functional unit in the kidney. Each kidney contains approximately one million of these structures. The afferent vessel brings blood into the glomerulus which is a capillary network whose walls are semipermeable. These walls act as filters through which some of the water and crystalloidal components of the plasma pass into Bowman's capsule. Proteins, other colloids, and blood cells cannot pass through this filter and along with most of the plasma are carried out of the glomerulus by the efferent vessel. The process of filtration in the glomerulus is believed to be purely mechanical and is influenced by both blood pressure and osmotic pressure

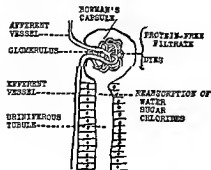


Fig 1—A Filtration Plant Diagram showing urine secretion. What is removed from the blood by the glomeruli? Courtesy, Hawk and Bergeim, "Physiological Chemistry," P Blakiston's Sons Co

The amount of glomerular filtrate formed each day is approximately 100 liters or about 100 times as great as the volume of finally excreted urine. This filtrate then passes through the uriniferous tubules which are long tortuous microscopic tubes lined with epithelial cells. In the tubule active reabsorption of water, glucose, amino acids, and salts occurs with little or no reabsorption of waste products. Those substances that are reabsorbed are spoken of as threshold substances whereas those that are not reabsorbed are called non threshold substances. This results in a very great concentration of the original dilute glomerular filtrate. The tubule cells also act in an excretory capacity and actually transfer certain material from the blood stream to the urine in the tubule. From the tubule the urine passes into larger collecting vessels and eventually leaves the kidney by the ureter and is stored in the bladder. In retrospect we see that there are three more or less independent phases to urine formation (1) glomerular filtration, (2) tubular reabsorption of water and useful constituents and (3) tubular excretion of additional waste products.

It is both interesting and instructive to note at this time that while the amounts of uric acid, urea, ammonia, creatinine, phosphate and sulfate are many times (25 to 100) as abundant in the urine as in the blood, the amount of chloride, sodium, calcium and magnesium remains roughly about the same, while in the case of glucose there is only a trace (about 0.05 per cent) in the urine and practically all of the sugar is reabsorbed.

### SELF-TESTING QUESTIONS

1. What are five paths of excretion?
2. Explain the process by which the kidneys secrete urine.
3. What substances are more abundant in the urine than in the blood?
4. What compound is largely recovered after filtration through the glomeruli?

## II. EXAMINATION OF URINE

### Importance of Urinalysis

Since the urine is the chief pathway for the elimination of waste products it is quite evident that the urine affords the physician or the nurse an interesting and helpful means of determining (1) whether normal metabolic changes are taking place, (2) whether abnormal waste products are being eliminated, and possibly some idea as to what may be the cause of these pathological changes, and (3) whether the kidneys are functioning close to optimum efficiency.

## Collection of Urine for Analysis

Emphasis should be placed upon the importance of collecting the *entire* 24 hour output, because metabolic changes taking place in the body at various times of the day produce different concentrations of the constituents in urine. However, the first specimen is better for *routine* analysis. The quantity of water and food consumed, and the amount of work done, in addition to many other factors (posture, stimulation, temperature, time of day, etc.) may cause wide variations in the *composition* of urine. Except in specific cases, random sampling is less valuable and may be quite misleading in certain cases. As a consequence the usual hospital procedure is to discard the early morning (8 A.M.) specimen of urine and collect all the urine passed during the next 24 hours. This quantity includes that passed the following morning at 8 A.M. To minimize or inhibit bacterial action, the urine is perhaps most satisfactorily preserved with toluene and kept under refrigeration. In case refrigeration is impossible, a thin layer of toluene over the surface of the urine is a quite satisfactory preservative that does not interfere with urinary tests. After measuring the total volume, a six ounce sample should be saved for analysis.

## Physical Examination of Urine

The *volume* of urine secreted during a 24 hour period may vary considerably because of the influence of many factors, particularly the *water intake*. The average adult (except when excessive fluid intake occurs due to overconsumption of beverages or to polydipsia) excretes from 1000 to 1500 ml of urine in 24 hours. In some countries where beer makes up a large part of the fluid diet the output is greater. Of the normal factors influencing urinary volume two of the most important are the *diet* (fluids as water, milk, coffee, soups) and *environmental temperature*. Vigorous exercise causes the sweat glands to secrete more perspiration and decreases the output of urine. Less perspiration in cold weather accounts for the greater urine volume in the colder months. High protein diet and drugs (caffeine in coffee, in tea) also increase this excretion. Drugs which increase the flow of urine are called *diuretics*. Frequently, the kidneys become impaired (nephritis) and there is difficulty in eliminating the inorganic and organic waste materials. At such times, the kidneys may excrete an increased volume of urine. Night urine from a normal person is about one half of that formed during the day. The significance of various changes in volume in health and disease follows.

<i>Normal</i>	<i>Abnormal</i>	<i>Significance</i>
1000 to 1500 ml (96 % H <sub>2</sub> O)		Depends upon water and fluid foods consumed, exercise, temperature, kidney function, nervousness, excitement, mental condition, etc
	High (polyuria)	Diabetes mellitus, diabetes insipidus, nervous diseases, certain types of chronic nephritis (kidney disorder), diuretics (drugs as caffeine, calomel, digitalis, alcohol, causing increased urinary excretion)
	Low (oliguria)	Acute nephritis, heart disease, fevers, eclampsia, diarrhea, vomiting
	None (anuria)	Uremia (urinary substances in the blood), acute nephritis metal poisoning, <i>e g</i> , due to bichloride of mercury

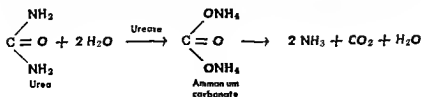
The color of normal urine is amber, the shade of yellow depending somewhat upon the concentration of the pigment *urochrome* and traces of other pigments. Very dilute urines are almost colorless because of the large water content. Normally the amount of urinary pigments varies little from day to day—regardless of the diet. A variety of colors is obtained in pathological conditions as observed in the following table

<i>Normal</i>	<i>Abnormal</i>	<i>Significance</i>
Yellow to amber		Depends upon concentration of pigment (urochrome)
	Pale	Diabetes insipidus, granular kidney, a very dilute urine
	Milky	Fat globules pus corpuscles in genitourinary infections
	Reddish	Blood pigments drugs food pigments
	Greenish	Bile pigment associated with jaundice
	Brown black	Poisoning (mercury, lead, phenol), hemorrhages, obstructive jaundice

A transparent and clear urine is normal when the sample is fresh, warm and of the proper dilution, but a precipitate of urates may appear on cooling and a precipitate of calcium phosphate may normally occur in an alkaline urine following a hearty meal. Turbidity occurring on standing for several hours may be caused by the precipitation of mucin. Variations in transparency and their significance follow

Normal	Abnormal	Significance
Clear		No significance
Cloudy on standing		Precipitation of mucin from urinary tract Not pathological
Turbid		Precipitation of calcium phosphate Not pathological
	Mulky (chyluria)	Presence of fat globules Pathological
	Turbid	Presence of pus as result of inflammation of the urinary tract Pathological

The odor of normal urine is faintly aromatic, probably due to certain volatile organic acids and an evil smelling substance called *urinod*. The odor of urines is also modified by the ingestion of certain drugs and vegetables. Asparagus, for example, imparts to urine a strong characteristic odor, caused by the presence of methyl mercaptan ( $\text{CH}_3\text{SH}$ ). Diabetic urine smells of acetone. The unpleasant ammoniacal odor of old unpreserved urine is brought about by bacterial action (urease) which changes urea into ammonium carbonate, and then into ammonia.



The significance of various changes in odor follows

<i>Normal</i>	<i>Abnormal</i>	<i>Significance</i>
Faintly aromatic		No significance
	Pleasant (sweet)	Acetone, associated with diabetes mellitus
	Unpleasant	Decomposition, or ingestion of certain drugs or foods

The *specific gravity* of normal urine averages about 1 020, depending upon the concentration of solid matter. Normal urine sp gr may vary from 1 010 to 1 030 and may be even lower following a large intake of water. The more dilute a urine the nearer the specific gravity approaches that of water. This condition of low specific gravity is prevalent when an unhealthy kidney finds difficulty in eliminating its salts, especially nitrogenous compounds. If the patient has *acute nephritis*, the urine is usually concentrated and the specific gravity is high, but if it is *chronic nephritis* then the kidney may excrete a greater volume of urine with a lower specific gravity. The specific gravity of the urine usually varies inversely as the volume, but in the case of *diabetes mellitus* this does not hold good, for then, both the specific gravity and the volume are high. The significance attached to an abnormal specific gravity follows

<i>Normal</i>	<i>Abnormal</i>	<i>Significance</i>
1 010 to 1 030 sp gr		Ordinarily, sp gr is inversely proportional to the volume
	Low	Dilution, if volume is large otherwise <i>chronic nephritis</i> , <i>diabetes insipidus</i>
	High	Concentrated if volume is small, otherwise if volume is large and light colored, <i>diabetes mellitus</i> . <i>Acute nephritis</i>

It should be pointed out that the specific gravity of urine in disease is rarely outside of the limits that may be obtained in a healthy individual. However, the excretion of a very dilute or very

concentrated urine by a healthy person can usually be associated with definitely altered intakes of fluid. Normally the kidneys can adjust specific gravity over the range from 1.000 to 1.030 depending on the relative amount of solid and water to be excreted. In kidney disease this power may be lost with the result that the kidney is not capable of adjusting the specific gravity which is spoken of as being "fixed." There are several clinical tests that are referred to as dilution-concentration tests that are designed to determine this function of the kidney. In general they may be carried out by having the patient ingest a large quantity of water and then not permitting any further water intake for 24 hours. Urine samples are collected at regularly spaced intervals. The normal response to such a test is that for a short time after the large intake of fluid the urine has a specific gravity approaching that of water but by the end of the 24-hour period the specific gravity is over 1.030. In contrast, a patient with kidney disease may be unable to excrete either a very dilute or a very concentrated urine.

A rapid clinical method of determining the specific gravity is the use of a urinometer. From the reading, a rough estimation of the total amount of solids per liter may be obtained by multiplying the numbers in the second and third place after the decimal point by 2.6 (Long's coefficient). For example, if the specific gravity is 1.021 the calculation would be

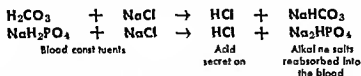
$$21 \times 2.6 = 54.6 \text{ gm per liter of urine}$$

The reaction of normal urine may be either acid or alkaline to litmus (pH 5.0 to 8.0) but is more frequently acid. This is caused mainly by the monosodium and potassium phosphates (e.g.,  $\text{NaH}_2\text{PO}_4$ ). The balance between the acid phosphate  $\text{NaH}_2\text{PO}_4$  and the basic phosphate  $\text{Na}_2\text{HPO}_4$  is one of many factors which influences the pH of urine, and makes the urine capable of becoming acid or alkaline to litmus. The ratio between these two phosphates in both the blood and the glomerular filtrate is approximately the same, but in the urine there is a greater influence exerted by the acid phosphate, probably because of the selective excretion of the acid phosphate or the reabsorption of some of the basic phosphate. In this way the kidneys aid in regulating the neutrality of the blood.

The acidity of urine increases somewhat if the diet consists largely of acid-forming foods (proteins). In certain diseases when the urine has a high acidity, a possible acidosis is suggested. This



of course can be confirmed or ruled out by blood chemical analysis. On the other hand, an alkaline urine may result from a vegetable diet, as in the urine of herbivorous animals. Citrus fruits produce an alkaline urine. It is interesting to note that the urine, after a heavy meal, may for some time remain neutral or even alkaline, which is known as the "alkaline tide." This is probably due to the increased demand during this time for acid radicals to form the hydrochloric acid of the gastric juice.



The withdrawal of hydrogen ions from the blood tends to cause its reaction to become more alkaline. However, the excretion of an alkaline urine will enable the blood reaction to remain more or less constant. The urine may also become alkaline as the result of eating fruits and vegetables which are rich in alkaline minerals and are known as alkaline ash foods. Ingestion of sodium bicarbonate and other "alkalizers" will also cause the urine to be alkaline. The persistence of an alkaline reaction in the urine of a patient on a mixed diet (e.g., animal and vegetable) points to probable infection of the bladder, providing that there has been no decomposition of the urine by putrefying bacteria. The significance of high acidity and an alkaline urine follows.

Normal	Abnormal	Significance
Acid (Slight)		Diet of acid forming foods (meats, eggs, prunes, wheat, etc.) overbalancing the base-forming foods (vegetables and fruits)
	High acidity	Acidosis, diabetes mellitus, many pathological disorders (fevers, starvation)
	Alkaline	Putrefying bacteria change urea into ammonium carbonate. Urinary infection or ingestion of alkaline compounds.

From the foregoing, it is evident that the kidney in excreting either an acid or alkaline urine is a very important part of the body machinery in keeping the blood plasma slightly alkaline.

## SELF-TESTING QUESTIONS

- 5 In what four ways may urine analysis be considered important?
- 6 How should *urina* be collected and preserved for analysis?
- 7 Why is random sampling of urine generally of little value?
- 8 What are the two most important factors influencing urinary excretion?
- 9 Name several conditions producing polyuria, oliguria, and anuria.
- 10 What is the significance of a urine that is pale milky, reddish, greenish, or brown black?
- 11 Why are milky and turbid urines generally considered pathological?
- 12 What is the significance of pleasant and unpleasant odors in urine?
- 13 How does the volume of urine excreted usually compare with its specific gravity? Name an exception to the general rule.
- 14 What compound causes an acid urine?
- 15 Explain how the kidney assists in regulating the neutrality of the blood.
- 16 Why may human urine be acid or alkaline?
- 17 What probably produces the condition known as 'the alkaline tide'?
- 18 What is the significance of a highly acid or alkaline urine?

## III. COMPOSITION OF URINE

The greater part of urine is water (96 per cent) in which are dissolved organic and inorganic waste products of the body. Of the organic matter, *urea* is the most important and abundant (approximately 50 per cent of solids), and is the principal nitrogenous end product of protein metabolism. Next to *urea* in abundance is the inorganic constituent, sodium chloride, which makes up ap-

<i>Constituent</i>	<i>Gm</i>
Water	1200.0
Solids	60.0
<i>Organic</i>	
Urea	30.0
Creatinine	1.2
Uric acid	0.7
Pigments etc.	trace
Urochroma	
Urobilin	
<i>Inorganic</i>	
Chlorides as NaCl	12.0
Sodium	4.0
Phosphates as $P_2O_5$	2.5
Sulfates as $SO_3$	2.0
Potassium	2.0
Ammonia (in salts)	0.7
Calcium	0.2
Magnesium	0.15

proximately 20 per cent of the solid matter. Since diet and other factors have such a great influence on the composition of urine any urinalysis will show wide variations from time to time. See the representative analysis on the preceding page showing the most important constituents of urine.

### Organic Constituents:

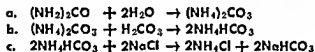
*Urea* is the chief end product of protein metabolism (exogenous) or of tissue protein metabolism (endogenous), and it contains the greatest part of the nitrogen found in the urine. Urea is found in nearly all of the fluids of the body, and some experiments seem to show that organs and tissues other than the liver can form urea. However, practically all of the urea is formed by the liver. The kidneys remove urea from the blood and excrete it into the urine. A small amount is excreted in the perspiration and saliva. The output of urea varies with the amount of protein eaten; a high protein diet such as meat produces an increased amount of urea. This output might be expected to be large when it is remembered that the body requires only a limited amount of protein for tissue building, that proteins in the usual sense cannot be stored in the body, and that any excess of proteins is finally decomposed, yielding energy and fuel and nitrogen waste products. A low urea output is usually associated with a low protein diet or advanced kidney disease.

*Ammonia* stands quantitatively next to urea as the most important nitrogenous constituent of protein metabolism (Fig. 2).



Fig. 2—Ammonium Urate. Spherule and thorn crystals. Metallic urates may occur in the sediment of acid urines. Name them. Courtesy, Hawk and Bergeim, "Physiological Chemistry," P. Blakiston's Sons Co.

The ammonia usually occurs as ammonium chloride, phosphate, or sulfate. The ammonia odor sometimes noticed in old urine is the result of fermentative bacteria changing urea to the unstable compound ammonium carbonate (p. 478). The importance of ammonia in abnormal metabolic changes is often attached to its use in neutralizing acids formed in excess of the amount which could be completely eliminated. For instance, in diabetes mellitus there is an increased amount of ammonium salts in the urine. This is the result of the urea acting as a source of an alkali capable of neutralizing certain organic acids (*e. g.*, acetoacetic and beta hydroxybutyric acids). Under these circumstances the following reactions occur:



From the equations the following facts can be indicated: (1) The bicarbonate formed in reaction c is available for neutralization of acid. (2) In the series of reactions producing bicarbonate, urea is used up and ammonium chloride is formed. This means that there are more ammonium salts and less urea to be excreted. Thus the ratio of urinary urea to urinary ammonium salts can be used as an indication of whether or not acidosis exists. (3) The reactions are in part responsible for the body's margin of safety in production against acidosis. (4) If alkalosis rather than acidosis is existent, then the reactions do not take place and practically no ammonium salts are excreted in the urine.



Fig. 3—Creatinine Colorless creatinine crystals. Of what value is a creatinine determination? Courtesy, Hawk and Bergeim, "Physiological Chemistry," P. Blakiston's Sons Co

In addition to the formation of ammonia from urea (p 478), it must not be overlooked that copious water drinking and acid forming foods (proteins) also increase the ammonia excretion, while on the other hand base forming foods (fruits and vegetables) decrease the amount of ammonia excreted

*Creatine* and its anhydride *creatinine* are both normal organic constituents of tissues, the former being especially abundant in muscle-tissue. Creatinine, but not creatine, is a product found in the normal urine of adults (Fig 3). Creatine is found only in the urine in children, in pregnant or menstruating women, and in such pathological conditions as fasting, fevers, diabetes, and diseases involving a condition of acidosis.

Although creatinine metabolism is not clearly understood, it is definitely known that creatinine is a product of creatine tissue metabolism (endogenous creatinine), and is related to the amount of muscle tissue in the body. The daily output of creatinine excreted remains so constant that the determined amount in a 24 hour sample serves to check this quantitative collection. An abnormal amount in the blood points to nephritis and uremia. In decided contrast to the quantity of urea, the amount of creatinine in the urine is independent of the protein ingested.

*Uric acid* represents a fairly small, but important, organic constituent of normal urine. Usually uric acid occurs in the form of salts called urates, and since these salts are insoluble in concentrated urines, they readily separate to form the largest part of the sediment of urine. Uric acid, unlike urea, does not come from ordinary protein metabolism, but from the destruction of nucleoproteins of foods or tissues. It may be recalled that the nucleoproteins are conjugated proteins formed by the reaction of nucleic acid with protein. They are an essential part of each cell, and upon hydrolysis and oxidation form a group of substances called purines, to which group uric acid belongs. A diet containing glandular organs (liver, kidneys, and sweetbreads) which are rich in cell nuclei, and also asparagus, spinach, and legumes will markedly increase the output of uric acid. Foods such as fruits, milk, eggs, and carbohydrates, however, give an almost purine or nuclein free diet, with the result that very little uric acid is formed. This is of decided value in the treatment of certain diseases (e g, gout) caused by the inability of the kidneys to eliminate uric acid properly. Being relatively insoluble (1 to 15,000), uric acid is excreted with difficulty. When there is some abnormal condition in uric

acid metabolism the amount of uric acid in the urine is decreased, while in the blood it is increased. At such times, the uric acid is deposited in the joints or affected tissues in the form of crystalline urates. To activate the kidneys and increase the uric acid output, such drugs as the salicylates, aspirin, and cinchophen have met with very doubtful success. Careful regulation of a purine free diet, plenty of drinking water, and exercise are perhaps of some assistance in the elimination of uric acid.

Sometimes there is too much destruction of nucleoproteins and a corresponding increase in the uric acid excreted. This would be true in malignant diseases resisting treatment (cancerous growths) in which the cells are destroyed, and also in leukemia where the leukocytes (white cells) are produced and destroyed in greater numbers.

The fact that uric acid has slight reducing properties makes Fehling's test for sugar in urine unreliable. However, uric acid will not reduce Nylander's reagent (bismuth subnitrate) or Benedict's solution, which reagents will show the test for sugar.

Pigments normally occurring in urine include urochrome, urobilin, and uroerythrin. Urochrome, the principal pigment, is a constant product of endogenous metabolism, but it is increased in fasting, in fevers, in hyperthyroidism and acid administration, and it is decreased during alkali administration. Urobilin is derived from the bile, and becomes of diagnostic value only when there is an increase due to liver disease. Uroerythrin imparts the pink to red color found in normal urine. It increases in various pathological conditions (fevers, liver disorders, digestive disturbances).

### Inorganic Salts

The inorganic or mineral constituents found in the urine are largely the chlorides, sulfates, or phosphates of sodium, potassium, calcium, and magnesium. Since they are the end products of food and tissue metabolism, or are obtained directly from the inorganic salts in the foods, the amount of these materials depends largely upon the variety and quantity of foods consumed. As stated, protein foods produce acid radicals, while vegetables, fruits, and milk tend to produce the basic ions.

Chlorides are next to urea in abundance of solid material in the urine. The principal chloride is sodium chloride, the excretion of which depends upon the chloride content of the food and the water consumed. In fasting, the percentage of salt in the urine runs low,

but it stays normal in the blood. A decrease in urinary chlorides is associated pathologically with the formation of exudates, e. g., in pneumonia, fevers and conditions involving edema.

*Sulfates* are mostly derived from the oxidation of certain proteins containing sulfur. In pathological conditions involving acute fevers, and during stimulated metabolism, the excretion of sulfates is increased, while a decrease is noted in disease involving a loss of appetite and lowered metabolism.

*Phosphates* are obtained from the inorganic phosphates in foods, and also from the oxidation of phosphorus organic compounds. The phosphates of the urine consist of  $\text{Na}_2\text{HPO}_4$ , and  $\text{NaH}_2\text{PO}_4$ , the latter salt accounting for the slight acid action of urine. As previously stated, these two salts act as buffers in maintaining the normal reactions of the body. An increase in the excretion of phosphate is connected with disease of bones (rickets, osteomalacia), pulmonary tuberculosis, diseases involving a decomposition of nervous tissue, and with water drinking, while a decrease is observed in pregnancy during fetal bone formation, in kidney diseases, in acute infectious diseases, and in febrile affections.

*Sodium and potassium* are always present in urine because of the sodium chloride and the potassium salts present in foods. Potassium chloride cannot be substituted for sodium chloride in the blood. The ratio of Na to K in urine is nearly five to three. An increase in potassium has been noted in conditions of acidosis and in fevers.

*Calcium and magnesium* are excreted principally in the feces and to a lesser extent in the urine. An excess of urinary calcium is associated with certain bone diseases (osteomalacia), while a low calcium content is prevalent in rickets. Since some magnesium is retained in osteomalacia while calcium is being lost, it is evident that the excretion of these two elements does not run parallel.

### Abnormal Constituents

In pathological conditions, abnormal constituents are found in the urine, the most frequent of which are proteins, glucose, acetone bodies, bile, blood, and pus.

*Proteins* being of a colloidal size are not capable of filtering through the kidney and consequently when found in the urine usually indicate nephritis. This permeable condition of the kidney permits protein to pass into the urine and results in a condition called *renal* or *true proteinuria* (or *albuminuria*) to distinguish it

from *accidental* albuminuria, in which latter condition the protein does not come from the blood, but is the result of injured cells of the urinary tract below the kidneys. In some diseases of the urinary tract, blood proteins and pus will respond to the usual protein tests (Heller's, Esbach's). Although protein in the urine indicates disturbances of the kidneys, it should be considered only in connection with other clinical findings. The simplest test for protein is the formation of a precipitate when urine is heated with a few drops of acetic acid, the acid dissolving any precipitated phosphates.

Acetone appears along with acetoacetic and  $\beta$  hydroxybutyric acids (acetone bodies). When found in the urine (a condition called acetonuria or ketonuria) it is the result of incomplete oxidation of fatty acids. Such a condition may be seen in healthy individuals when fasting, or with a high fat and a low carbohydrate diet, but it most often appears in diabetes mellitus and during high fevers. In very severe forms of diabetes, the alkaline reserve of the blood is so depleted by these acids that a fatal acidosis may develop. Since ammonia is a reserve supply of alkali (formed at the expense of the urea), a considerable part of the acids formed are found in the urine as ammonium salts of these acids, and since acetoacetic acid readily changes into acetone, the usual tests are made for acetone. Rothera's test for acetone and acetoacetic acid occurs on p. 754.

Glucose in more than mere traces in the urine is considered pathological and this condition is known as *glycosuria* (sugar in the urine). However, glucose may be excreted in the urine because of a low renal threshold, giving rise to so called *renal glycosuria*. One type called *temporary glycosuria* is the result of the ingestion of more sugar than the body can store at one time, the average glucose tolerance being around 50 Gm. per dose without producing glycosuria. Temporary glycosuria may occur during vigorous exercise, or strong emotions such as worry, or excitement, which latter condition may possibly be due to oversecretion of epinephrine by the suprarenal or adrenal glands. The other type called *permanent glycosuria* (diabetes mellitus where there may be as much as 10 per cent of sugar found in the urine) is not caused by a disease of the kidneys but rather by a lack of insulin or the inability of the body to store and burn glucose properly, with the result that sugar retained in the blood stream is very high and large amounts are excreted in the urine. As has been previously stated, one test (Benedict's, p. 329) for glucose is based upon its ability to reduce



metallic hydroxides in an alkaline solution, and may be distinguished from lactose by the fact that lactose does not undergo fermentation with baker's yeast.\*

*Lactose* has been found in the urine during pregnancy and lactation, but does not apparently have any pathological significance.

*Bile pigments* produce a yellowish green to brown color in urine which upon shaking readily produces a foam of a yellowish cast. Pathologically, the excessive production of bile or obstruction to its excretion into the intestine gives rise to jaundice. The bile then stains various tissues of the body. The tests for bile depend upon oxidation of the pigments to form various colors (green, blue, yellow) appearing as rings at the point where the reagents meet in the test tube.

*Blood* may occur in the urine (hematuria) because of a lesion in either the kidney or in the urinary tract below the kidney. Also when hemolysis of the blood corpuscles takes place (laking of erythrocytes) the blood pigment passes into the urine (hemoglobinuria). This latter condition may occur in scurvy, malaria, in severe burns, in some types of poisoning, in transfusing blood that undergoes hemolysis in the patient's blood, and in other pathological conditions. The most delicate test for blood is a blue color produced by the benzidine test (see laboratory experiment, p. 754).

*Indican in excess* is indicative of excessive intestinal putrefaction, and is the result of detoxication of indoxyl which results from putrefactive changes of the amino acid tryptophan. Obermayer's test for indican occurs on p. 755.

*Pus* usually develops in inflammatory conditions, such as catarrh of the bladder, inflammation of the pelvis of the kidney, and inflammation of the urethra, or in abscesses of the urinary tract. Pus in the urine is known as *pyuria*. In a broad sense, a pus cell is a dead leukocyte. Pus cells may be detected under the microscope; they appear as round, colorless, nucleated cells.

**SEDIMENT:** A microscopic examination of the sediment of pathological specimens is quite helpful in diagnosis and prognosis. Although the sediment may be collected by allowing the urine to stand for many hours, it is much quicker and more satisfactory to remove the sediment by centrifuging the urine. Perhaps the most

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\* There are at the present time several commercial preparations available for the detection of sugar in the urine. The most widely used of these is "Clinitest" which is based on the copper reducing properties of glucose in hot alkaline solutions. In this test a small tablet, containing copper and alkali and a mixture to generate heat when the tablet dissolves, is dropped into a small quantity of urine and in the presence of glucose the mixture takes on an orange color due to reduced copper.

important elements in the sediment decompose on standing, so that unless the specimen is centrifuged much of the diagnostic value of the examination is lost. The sediment will fall under two classes first, the *unorganized*, containing calcium phosphate, uric acid and the urates, and the second, the *organized*, containing the epithelial cells, pus cells, cylindroids, and casts. An occasional red cell may be present but an increased number indicates a pathological condition.

<i>Unorganized</i>	<i>Organized</i>
Calcium phosphate Uric acid Urates, etc Sulfonamide crystals in patients receiving the drug	Epithelial cells Pus cells cylindroids Casts etc

Normal urine upon standing generally produces unorganized sediment, which dissolves upon warming, diluting, and adding a few drops of dilute hydrochloric acid, provided that only phosphates or urates are present. Uric acid sediment is soluble in sodium hydroxide. In the presence of organized sediment, heat will probably coagulate the protein. Moreover, hydrochloric acid may precipitate the protein and destroy the casts, while sodium hydroxide not only dissolves mucous cells with the formation of a clear solution but also makes the pus gather into a thick, sticky mass. In addition, treatment with sodium hydroxide also destroys any microorganisms present as evidenced by the production of a milky appearing urine which cannot be clarified by filtration.

An increased number of epithelial and pus cells is frequently present in specimens from females (who have leukorrhea), other wise they indicate some disturbance along the urinary tract, although a small number may not be pathological. Much pus indicates bacterial infection as in venereal diseases and renal abscesses. Sometimes the kidney tubules become packed with protein and other material to form a cylindrical mass. Upon being discharged the mass retains the shape of the tubules to form what are called casts, and indicate some kidney disturbance, whether albumin is present or not. The expelled protein mass may tear loose some kidney cells and produce hemorrhage.

### Urinary Calculi:

Sometimes the mineral salts precipitate in such large and compact masses in the urinary tract to form stones, called *calculi*, although the process is a gradual one. An examination of these stones shows that mineral constituents mostly have been deposited in concentric layers on a nucleus of epithelial debris, a blood clot, or more likely uric acid or urate crystals. Generally, the calculi are voided without any difficulty before they have become very large, but when lodged in the pelvis of the kidney, or in the duct (ureter) that carries the urine from the kidney to the bladder or in the bladder, they may be very large, sometimes weighing from



Fig. 4—Casts. Cylindrical molds of uriniferous tubules forced out by the pressure of the urine flow. h, hyaline cast, g, granular cast, w, waxy cast, e, epithelial cast. What does the finding of casts indicate?

1 to 50 Gm. or even more. The color, form, hardness, and composition of the calculi vary greatly, according to the diet and the acid condition of the urine as well as the cause. Calculi are more apt to form when there is: (1) A highly concentrated urine, and (2) an abnormal amount of uric acid eliminated, (3) genitourinary infection, (4) a shortage of protective colloid (such as hyaluronic acid) in the dispersion of urinary crystalloids.

Chronic vitamin A deficiency in rats is associated with degenerative changes in the kidneys and calculus formation. In fact, experimentally, this is the most effective way of producing stones in the urinary tract. It is believed that infection sets in, producing stasis\* and decomposition of the urine, making it alkaline and precipitating salts which form calculi.

\* Stasis is the arrest of the blood current due, presumably, to abnormal resistance of the capillary walls

## SELF-TESTING QUESTIONS

- 19 What is the significance of a low urea output?
- 20 How is ammonia formed and what is its importance in the urine?
- 21 What is a guide to the severity of acidosis?
- 22 What significance is attached to the presence of creatinine?
- 23 What foods increase and what foods decrease uric acid formation?
- 24 Explain how uric acid in the form of urates produces pain in the joints in such a disease as gout.
- 25 How may uric acid elimination be increased?
- 26 What are three important urine pigments?
- 27 What is the significance of decreased chlorides? of increased sulfates? of decreased and increased phosphates? of increased potassium? of decreased and increased calcium in the urine?
- 28 How would you distinguish between renal and accidental proteinuria?
- 29 In what metabolic disturbances is acetone produced?
- 30 What is the distinction between temporary and permanent glycosuria?
- 31 What is the significance of bile, blood pus casts and calculi in the urine?

## SUGGESTED ACTIVITIES

### I THOUGHT PROVOKING QUESTIONS

- 1 What happens to the health of a patient when carbohydrates are withdrawn from the diet?
- 2 How should the diet of diabetics differ from that of nephritics? Give reasons for your answer.
- 3 If a diabetic on entering the hospital has acidosis how may you account for the condition? What measures should be taken to relieve it?
- 4 If the elimination of nitrogen in waste materials of the urine exceeds the intake of nitrogen in the proteins of the diet, what conclusions would you draw? How could this condition be remedied?
- 5 What happens in the tissues when the intake of food exceeds the needs of the body? When it is insufficient? By what means may we determine these facts?
- 6 What are the disadvantages of eating an excessive amount of protein? The advantages if any.
- 7 Name several circumstances under which the need for mineral matter is greater than usual. Describe the results when this need is not supplied.
- 8 In what respect does the metabolism of a diabetic differ from that of normal persons? Describe how this modifies his use of food and how the diet should be modified.
- 9 Discuss the advantages and disadvantages of milk as a food for infant feeding.
- 10 Following the discovery of sugar in the urine what other condition should be present before diagnosing diabetes?

11 How are the composition and properties of urine modified by the following

- |   |   |
|---|---|
| (a) Exercise?   | (k) Injury to cells of urinary tract?   |
| (b) High protein diet?                                    | (l) High fat and low carbohydrate diet? |
| (c) Acute nephritis?                                      | (m) High fevers, diabetes?              |
| (d) Chronic nephritis?                                    | (n) Eating $\frac{1}{2}$ lb of candy?   |
| (e) Diabetes?   | (o) Jaundice?                           |
| (f) Vegetable diet, fruit, nuts milk?                     | (p) Lesions in kidney or urinary tract? |
| (g) Injection of baking soda?                             | (q) Inflammatory conditions?            |
| (h) Starvation?   | (r) Infection of the urinary tract?     |
| (i) Eating glandular organs (liver, kidneys sweetbreads)? |   |
| (j) Bone diseases?  |   |

12 What condition would most likely be indicated by each of the following urinalyses?

Volume	Color	Sp Gr	Sugar	Protein	Acetone	Acid	Alkaline	Costs	Pus	Bile	Sediment	Blood	Indican in Excess
Large			+	-									
Large			-	+									
Small				+				+				+	
Small	Dark Yellow										+ on standing clears on heating		
			+		+	High			-				
											clears on acidifying		
							+		+			+	
	Gr Br Yellow Foam									+			+

## II VOCABULARY TESTING OF NEW TERMS

polyuria	urochrome	acetonuria
oliguria	urinometer	hemoglobinuria
anuria	"alkaline tide"	casts
chyluria	albuminuria	urinary calculi
proteinuria	ketonuria	pyuria

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Value of Urinalysis in Diagnosis
- 2 The Organs of Excretion What They Accomplish
- 3 How the Kidneys Function in Urine Formation

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on pages 749, 752

## CHEMICAL CHANGES IN THE TISSUES

## CHAPTER OUTLINE

- |   |  |
|---|--|
| <p><b>I METABOLISM</b></p> <p>(a) Chemical nature of metabolism</p> <p>(b) Energy metabolism</p>  | <p>(b) Oxidation of fats</p> <p>(c) Incomplete fat metabolism</p> <p>(d) Ketosis and antiketosis</p>   |
| <p><b>II BASAL METABOLISM</b></p> <p>(a) Determination of basal metabolism</p> <p>(b) Internal factors affecting basal metabolic rate</p> <p>(c) Variation in weight</p> <p>(d) Variation in height</p> <p>(e) Variation in age</p> <p>(f) Variation in sex</p> <p>(g) Variation of internal secretions</p> <p>(h) Specific dynamic action of foods</p> <p>(i) Practical value of ascertaining the metabolic rate</p> | <p><b>V METABOLISM OF PROTEINS</b></p> <p>(a) Function of amino acids</p> <p>(b) Oxidative deamination</p> <p>(c) Transamination</p> <p>(d) Urea formation</p> <p>(e) Nitrogen balance</p>   |
| <p><b>III METABOLISM OF CARBOHYDRATES</b></p> <p>(a) The high energy bond</p> <p>(b) Changes produced by the liver</p> <p>(c) Anaerobic catabolism</p> <p style="padding-left: 20px;">glycolysis</p> <p>(d) The aerobic phase</p> <p style="padding-left: 20px;">tricarboxylic acid cycle</p> <p>(e) Conversion of glucose to fat</p> <p>(f) Carbohydrate tolerance</p>   | <p><b>VI METABOLISM OF INORGANIC SALTS</b></p> <p>(a) Classification of inorganic (ash) elements</p> <p>(b) General functions of inorganic salts</p> <p>(c) Control of contraction of muscles and irritability of nerves</p> <p>(d) Maintenance of osmotic pressure</p> <p>(e) Role in acidity and alkalinity of digestive juices</p> <p>(f) Preservation of normal chemical reactions</p> |
| <p><b>IV METABOLISM OF FATS</b></p> <p>(a) Function of fats</p>   | <p><b>VII METABOLISM OF WATER</b></p> <p>(a) Adaptation of life to water</p> <p>(b) Water exchange</p> <p>(c) Water needs</p>  |

## I. METABOLISM

## Chemical Nature of Metabolism:

There are many different manifestations of life exhibited by the cells, involving a correspondingly large number of chemical changes which are always accompanied by energy changes. The general expression used for the sum of all these energy changes is *metabolism*, which in a restricted sense is defined as the rate of the oxidation processes.

The word "metabolism" involves two phases of chemical reactions, the building up process called *anabolism* and the tearing down process, called *catabolism*. Anabolism, or constructive metabolism, refers to the building up of body tissues and reserve nutrients stored in the body. Catabolism, or destructive metabolism, refers

to the breaking down of discarded body cells and waste products. The anabolic and catabolic processes during normal adult life usually balance each other, the constructive processes equalling the destructive ones. In youth or during a convalescent period, anabolic functions may be greater, while in old age, disease, violent exercise, and malnutrition, catabolism is more preponderant.

Cells vary markedly in their specific functions, even though all cells have access to the same supply of food carried by the blood. The selective power of each cell is such that it takes only what it may assimilate, rejects what may not be used, and thus selective power represents one of the mysteries of life. There are differences in concentrations of various substances between the inside and outside of the cell. Of the many substances taken into the cell, oxygen is of utmost importance, since it is a vital factor in almost all metabolic changes. The use of oxygen in the body makes possible the production of energy of which the greater part (four fifths) appears as heat. It is interesting to note that Lavoisier was the first to study the role of oxygen in generating heat and potential energy of the body. He made a chemical study of the respiration of living forms, finding that the life of an animal, like a candle's flame, was dependent upon the continual removal of oxygen from the atmosphere, and upon the return of an equivalent quantity of carbon dioxide. He found, moreover, that the amount of oxygen consumed was related to the amount of heat developed by the animal. Life, declared Lavoisier, is a chemical process akin to combustion. This was an epoch making discovery.

### Energy Metabolism

The carbohydrates, fats, and proteins can be used equally well to supply fuel for heat and mechanical energy. The proteins are unique, however, in that they alone are capable of restoring or building new body tissue. This is readily understandable when we recall that most functional body tissue is of a protein nature and that proteins contain nitrogen whereas fats and carbohydrates do not.

Energy is expressed in terms of units of heat. The amount of heat required to raise the temperature of 1 Gm. of water  $1^{\circ}\text{C}$  is called a calorie. However, to measure the energy changes of the body it is more convenient to select a heat unit 1000 times as large called the large Calorie (capital C) or kilocalorie, which is the amount of heat required to raise the temperature of 1000 Gm.

(1 kg) of water  $1^{\circ}\text{C}$  The caloric value of a food is determined by placing a weighed quantity in a bomb calorimeter (Fig 1), filling the bomb with oxygen under pressure, closing, and immersing the bomb in a weighed quantity of water The food is then ignited by an electric current, and the rise in temperature of the water is measured By means of this instrument the physiological fuel values of foods show that

1 Gm of carbohydrates produces 4.1 Calories

1 Gm of fats produces 9.1 Calories

1 Gm of proteins produces 4.1 Calories

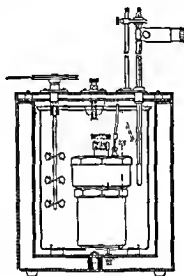


Fig 1—Food Values Determined with a Calorimeter The cross section of the calorimeter shows the calorimeter bomb immersed in water in which is a stirrer and thermometer Why is the heat obtained in the calorimeter slightly higher than that shown for the oxidation of a food in the body?

For convenience these values usually are used as whole numbers as follows carbohydrates, 4 Cal /Gm , fats, 9 Cal /Gm , and proteins 4 Cal /Gm

From these values the caloric value of any food may be estimated For instance, in the following example 100 Gm of milk furnishes 68 Calories

Food	Per Cent Analysis		Calories per Gram		Total Calories
Carbohydrate	5	X	4	=	20
Fat	4	X	9	=	36
Protein	3	X	4	=	12



Various proportions of the three principal foodstuffs for daily requirements have been suggested, a favored one being that of the German physiologist, Voit. He proposed 500 Gm of carbohydrates, 56 Gm of fat, and 118 Gm. of protein. Such a diet would furnish approximately 3000 Calories, an amount sufficient for a normal adult engaged in ordinary activities. The exact protein requirement has been seriously debated by many investigators. The current views appear to indicate that 80 to 90 grams of any



Fig 2—Giving a Basal Metabolism Test. The amount of oxygen consumed is used in calculating how much food is being oxidized or the number of calories of energy produced. This amount of energy (basal metabolism) is compared with a chart, showing the average normal metabolic rate for a person of the same height, weight, age, and sex. What do you think would be the practical value of ascertaining the metabolic rate? *Courtesy, Sanborn Company*

good protein per day is quite adequate for a healthy adult. Recently it has been shown that in many diseases an increased intake of protein is quite beneficial.

### SELF-TESTING QUESTIONS

1. What is meant by metabolism? Anabolism? Catabolism?
2. How is the caloric value of a food determined?
3. What are the physiological fuel values of carbohydrates, fats and proteins?

## II. BASAL METABOLISM

### Determination of Basal Metabolism

The consumption of food as well as the activity of the body varies. It follows that the energy demand made on the body (or the cells composing it) must also vary from time to time. The harder the physical work, the greater the amount of heat produced by the body. At complete mental and physical rest and in the absence of food in the stomach and intestines, certain basic energy changes in the cells are still going on, otherwise there would be no life, but these energy changes are at a minimum. At such times, the body may be likened to an idling automobile—ready to perform work at a moment's notice. *This minimum amount of energy required to maintain life when the body is at rest, at normal temperature, and when no digestion is going on is known as the basal metabolic rate (BMR).*

Under such conditions the energy requirement, measured as the amount of heat evolved in large Calories per 24 hours per sq. meter of body area, called the *basal metabolic rate*, is a gauge of the speed at which metabolic processes are taking place. To produce this energy transformation without ingested foodstuffs means that chemical reactions are taking place on the food stored in the body, chiefly fats and carbohydrates. Since there is a definite relation between energy production and oxygen consumption the usual clinical method of obtaining the basal metabolic rate is to determine the amount of oxygen consumed by a patient (who has been properly prepared) during a period of six to eight minutes (Fig. 3). The average oxygen consumption per minute is then estimated. From this the 24-hour oxygen requirement is easily calculated. The amount of oxygen consumed is used in calculating how much food is being oxidized, or the number of Calories of energy produced. This amount of energy, the basal metabolic

rate, is compared with a chart showing the average normal basal metabolic rate for a person of the same height weight, age and sex. Any variations from the normal are reported as *percentage* variations plus or minus  $-10$  meaning 10 per cent below the normal,  $+10$  meaning 10 per cent above normal. The normal basal metabolism of an adult male of average size and about thirty five years of age is 39.5 Calories per square meter per hour. For a body area of 1.8 square meters this represents a basal metabolism of approximately 1700 Calories per day. The basal metabolic rate of a normal person before breakfast is so constant that a variation from normal of more than 15 per cent is indicative of some disturbance in the vital processes.

These facts are fundamental in dietetics, for they mean that an adult confined to bed would need 1700 Calories even if he never turned over or lifted a hand.



Fig. 3—The Benedict-Rath Metabolism Apparatus. Note in the illustration how the apparatus also makes a graphic chart record of the patient's oxygen consumption. Courtesy Warren E. Collins, Inc.

### **Internal Factors Affecting the Basal Metabolic Rate:**

There are many factors that must be considered in carrying out a basal metabolic determination. Such external factors as exercise, eating or fasting can be controlled in making a basal metabolic test but not such inherent factors as weight, height, age, sex, and internal secretions. All must be taken into account in estimating the significance and the value of the basal metabolic rate (B.M.R.).

#### **Variation in Weight:**

In two men of the same height, one distinctly thin and one fat, it has been found that a smaller amount of heat will radiate from the thin man. For this reason consideration must be given to the surface area of the body.

#### **Variation in Height:**

The same reasoning shows that two men of the same weight, but differing in height, will have different amounts of heat radiation, height increasing the heat radiation.

#### **Variation in Age:**

Of considerable interest is the effect of age on the basal metabolic rate, the production of heat being greater in youth than in old age. During physical growth increased height and weight may sometimes counterbalance a difference in age. For instance, a youth of 12 years of age might have the same production of energy as one 16 years old. The latter's increased height and weight may at times counterbalance a decreased energy production.

#### **Variation in Sex:**

Another interesting fact is that for some reason (probably more fat and less muscle in the female) the basal metabolic rate of women is about 10 per cent lower than that of men of the same height, weight, and age. This is so because B.M.R. measures "active" protoplasm, and fat is not very active tissue.

#### **Variation of Internal Secretions:**

The internal secretions, or hormones, of certain glands (endocrine) stimulate body tissues, and in this way markedly influence the basal metabolic rate. For instance, the adrenal glands may affect blood pressure, the pituitary glands influence growth, the Islands of Langerhans control sugar metabolism, and the secretion

of the thyroid gland increases the rate of oxidation. Feeding thyroid tissue or thyroid extract to any animal (including man) always raises the B M R. When the thyroid gland produces more secretion than is required by the normal body, a disease known as *hyperthyroidism* develops and the basal metabolic rate must always be above normal in this disease.

Recent work on animals has shown that certain fractions of the pituitary gland have a profound influence on the basal metabolic rate. A potent extract may produce a marked increase in B M R.

### Specific Dynamic Action of Foods

Ingested foods speed up oxidative reactions in the tissues to produce energy. In other words foods stimulate the rate of metabolism, the effect being referred to as the *specific dynamic action* of food. Of the different foods proteins have by far the greater and more prolonged specific dynamic effect. To maintain the oxidative reactions in the tissues, that is, to supply the energy required to metabolize foods, it has been estimated that on an average mixed diet over 10 per cent of the total food Calories used must be added to the basal requirement in order to take care of this specific dynamic effect. Therefore, a daily energy requirement embodies the basal energy requirement, the energy for muscular activity, and the energy for the specific dynamic action during metabolism.

### Practical Value of Ascertaining the Metabolic Rate

Since under normal conditions the metabolism remains fairly constant from day to day, any marked variation will be of definite clinical assistance in diagnosing certain pathological states. This is especially true in the diagnosis and prognosis of goiter. In fact, several metabolic disturbances are associated with over or under secretion of the thyroid gland. A lack of this secretion (*hypothyroidism*) may result in a gain in weight, apathy, muscular weakness, perspiration, and flushing of the skin, while an excess secretion (*hyperthyroidism*) produces an increased heart rate and respiration rate, excitability, bulging of eyes, etc.

In addition to the clinical value of ascertaining the basal metabolic rate in certain diseases, it has some practical use in determining the dietary requirements of those who are overweight or underweight. The basal metabolic rate furnishes reliable information for estimating the food requirements of overweight or underweight

people. The basal metabolic rate, like body temperature and blood pressure, is an additional tool which permits the physician to recognize certain types of disease.

The value of the basal metabolic rate is shown by the table of selected pathological conditions on page 504.

### SELF-TESTING QUESTIONS

4. What is the meaning of basal metabolic rate? How is it determined? How is it read?
5. What internal factors affect metabolism?
6. Explain one possible difference in the metabolism of two men of the same height of same weight of different ages.
7. How does the secretion of the thyroid gland affect the basal metabolism (BMR)?
8. What clinical and practical value has the basal metabolic rate determination?

### III. METABOLISM OF CARBOHYDRATES

The nutrients from the digestion and absorption of foods, together with oxygen, are supplied by the circulation of the blood to the organs and tissues. Here they are used for the production of energy and also for the synthesis of the many substances required by the body, both for its structure and its functioning. The utilization of nutrients to satisfy body requirements invariably involves a series of chemical transformations. For illustration, as will be discussed later, when glucose serves as a source of energy it is not oxidized directly, in one step, to the end products carbon dioxide and water. Rather, it goes through a series of gradual changes so that there are numerous related intermediate steps and intermediate compounds. This is known as *intermediary metabolism*. This field of biochemistry is being intensively explored, and the discoveries made have been and will continue increasingly to be of great value in coping with disorders of the human body.

The metabolism of carbohydrates, like that of lipids and proteins, is controlled by enzymes and coenzymes, hormones, minerals (as ions), and other factors. It is known that some of the vitamins play an essential role in metabolism since they are required for the synthesis of certain enzyme systems.

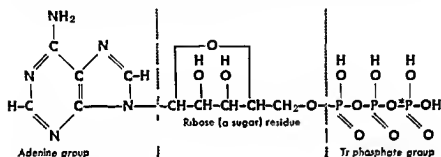
#### The High Energy Bond

It is now generally accepted that the immediate source of energy for muscular activity is a compound called adenosine triphosphate, abbreviated ATP. This substance, present in all muscle tissue,

Known or Suspected Pathological Condition*	Range of B M R	Accepted Treatment (See references)	Value of B M R
Exophthalmic Goiter	High +15 to +75 and over	Full iodination followed by subtotal thyroidectomy. Administration of thyroidal or radiation successful in some cases. ( <i>J H. Means Thyroid and Its Diseases</i> p 405)	Metabolism tests help to confirm diagnosis and determine safe operation risk on basis of iodine response. <i>After of some prognosis help in medical regimen.</i>
Toxic Adenoma	High, +20 to +75 and over	Surgical. Induced salt most effective prophylaxis ( <i>Ibid</i> p 104)	Differential diagnosis from mild toxic goiter is sometimes required especially in patients with normally low rates. Best accomplished by diagnostic tests with iodine measuring results with metabolism tests. ( <i>Ibid</i> p 178)
Simple (Colloid) Goiter	Normal -10 to +15	Thyroid (U.S.P.) 1½ gr daily	Repeated metabolism tests together with clinical examination helpful in checking efficacy of treatment.
Myxedema	Low -15 to -45	Dried thyroid (U.S.P.) gland by mouth ( <i>Ibid</i> p 253) Dose 1½ gr to 3 gr daily	
Ovulation (Early diagnosis imperative for satisfactory result)	Low -15 to -45	Thyroid (U.S.P.) ( <i>Ibid</i> p 271) ½ gr to 1½ gr depending on age.	B M R useful with clinical manifestations in establishing correct dosage of thyroid ( <i>Ibid</i> p 272)
Pituitary Disturbances { Acromegaly Hypopituitarism	Normal to raised +10 to +50 Low late in disease (-20) Normal to lowered +10 to -20	If metabolism test shows elevated rate iodine may be effective to some extent. ( <i>Ibid</i> p 113 E F Du Bois, <i>Basal Metabolism in Health and Disease</i> p 377) Possibility of effectiveness of several types of hormones depending on pituitary deficiency type ( <i>J H. Means Thyroid and Its Diseases</i> p 531)	
Obesity { Exogenous Endogenous	Normal to high -10 to +20 Normal to low +10 to -20	Diet restrictions and exercise ( <i>Ibid</i> p 524) If test shows B M R is normal, thyroid extract will be of no value. Pituitary extract (anterior lobe) sometimes helpful ( <i>Ibid</i> p 526)	Thyroid extract sometimes used, but requires careful checking of results by metabolism tests as it may cause hyperthyroidism. ( <i>Ibid</i> p 525)
Nervous and Mental Disorders	Normal to low +10 to -30	As required by and visual. Reaction of nervous patients with low rates to thyroid very varied and unpredictable ( <i>Ibid</i> p 533) As for hyperthyroidism. (Work now being done on treatment of congestive heart failure and angina pectoris by thyroidectomy ( <i>Ibid</i> p 542)	Metabolism test helpful in differentiating thyrotoxic nervousness from true effort syndrome
Thyroid Heart	Normal to raised -10 to +30		B M R will help to differentiate thyrotoxic heart from true heart disease or thyrotoxicosis superimposed on heart disease

\* Courtesy Sanborn Co. Cambridge Mass

can release considerable energy through a reaction of hydrolysis which produces adenosine diphosphate, abbreviated ADP, and phosphoric acid. Adenosine triphosphate is said to have a high energy linkage in its structure. ATP serves also as a source of the energy needed for promoting some of the chemical reactions of intermediary metabolism, and as a source of the phosphate group for a number of phosphorylations. The chemical structure assigned to this highly important and interesting compound follows. The two vertical broken lines through the formula are merely to show the three structures which are incorporated in the ATP molecule.



The \* indicates the high energy bond. Hydrolysis breaks this bond to release energy and to form ADP and  $\text{H}_3\text{PO}_4$ .

Much of the energy released in the catabolism of nutrients is stored in muscle tissue as ATP, where it is immediately available for muscular activity.

### Changes Produced by the Liver.

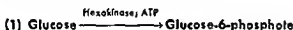
In the course of digestion the carbohydrates are changed into the monosaccharides, *glucose*, *fructose*, and *galactose*, which, after absorption into the capillaries of the intestinal mucosa, are carried by the blood to the portal vein, and thence to the liver. After the blood passes through the liver into the hepatic vein two changes are noticed: (a) glucose is the only sugar present, and (b) of more importance its amount has been decreased. This decrease in sugar content is accounted for by the condensation of the monosaccharide molecules under the influence of a group of enzymes to form the polysaccharide "glycogen." This is known as animal starch and is stored as a colloidal and indiffusible product in the liver.

The liver, then, is a very important organ in carbohydrate metabolism since it regulates the amount of glucose which enters



the general circulation to be carried to the tissues. This is only one of the many vital functions of the liver. Even though at times the consumption of carbohydrates becomes so large that the sugar content of the portal vein may be twice the normal amount, the liver removes the excess and stores it as glycogen. The excess sugar which is stored temporarily in the liver as glycogen can be changed by enzymes at a moment's notice into glucose for the purpose of oxidation in the tissues during fasting. Some glycogen is also found in the tissues, but even that amount, together with glycogen of the liver, does not normally total one pound. This would be consumed in one day of fasting. Therefore it is evident that glycogen provides only a temporary and limited reserve supply of fuel for energy or for muscular work, and for maintaining a somewhat constant glucose concentration in the blood.

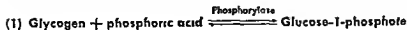
In the liver the synthesis of glycogen from glucose, called *glycogenesis*, proceeds as follows:

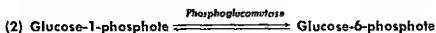


The numbers used in some of these names identify carbon atoms in the carbon chain of the molecule. Glucose has a chain of six carbons. The numbering starts with the carbon of the aldehyde end of the chain. Thus in glucose 1 phosphate a phosphate group is joined to carbon number one by an ester linkage.

A series of reactions similar, if not identical, to those just given occurs when muscle glycogen is formed from glucose withdrawn from the blood. The first of these reactions is not reversible, it progresses only because of the high energy provided by ATP, which serves also as the phosphorylating agent.

When liver glycogen is hydrolyzed to produce glucose, a process called *glycogenolysis*, the following reactions occur:





When glycogenolysis takes place in muscle tissue, only the first two of the above three reactions take place. Muscle tissue contains no phosphatase (glucose 6 phosphatase) to hydrolyze the glucose-6 phosphate.

At least two hormones, epinephrine and insulin, play a part in glycogenesis and glycogenolysis. It may well be that these hormones control the activity of the enzymes hexokinase and phosphorylase. Insulin promotes the conversion of blood sugar to glycogen (glycogenesis) while epinephrine has the opposite activity, favoring the hydrolysis of glycogen. Thus if the injection of too much insulin into a diabetic patient produces hypoglycemia (low sugar), epinephrine can be used to increase the blood sugar and relieve insulin shock.

All of the nutritionally important simple sugars, fructose and galactose as well as glucose, can undergo glycogenesis, but glycogenolysis produces glucose only.

### Anaerobic Catabolism; Glycolysis

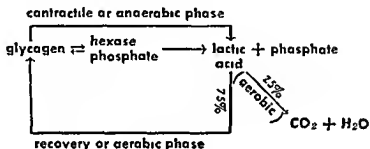
Having noted the part played by the liver in glycogenesis and glycogenolysis we shall next examine the manner in which glucose (blood sugar) breaks down in the liver, and especially in muscle tissues, to release energy. For purposes of discussion this is considered in two stages, first the *anaerobic phase* (without air, i. e. oxygen) and second the *aerobic phase* (in presence of air).

The anaerobic phase of the catabolism is known also as *glycolysis*. It includes a series of chemical changes which split the six carbon atom glucose molecule into two molecules of three carbons each. Reactions in the series are controlled, i. e., catalyzed, by specific enzymes. The diagram on p. 508 outlines glycolysis, starting with the glucose which is present in liver and muscle tissue, or which becomes quickly available from glycogen through glycogenolysis.

In this series of changes, two molecules of ATP are consumed and four are produced for each molecule of glucose metabolized to pyruvic acid. This is a net gain of two molecules of ATP, which with high energy bonds represents a storage of energy released in glycolysis.



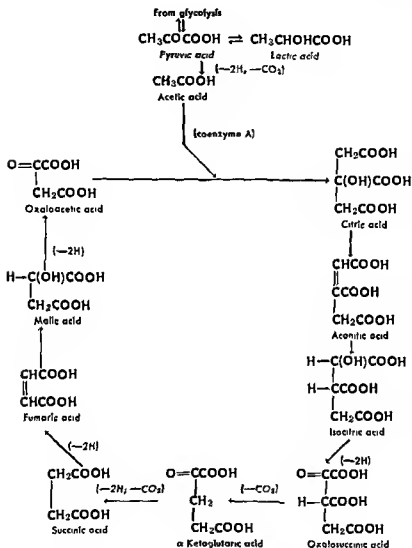
The lactic acid which is produced in the anaerobic phase from pyruvic acid must be promptly disposed of. A considerable amount is resynthesized to glycogen during the recovery period following exercise. Particularly after strenuous exercising, lactic acid diffuses from the muscle tissues into the blood, and a small amount of this is excreted in the urine. The larger part is returned to the liver where it is converted to glycogen. Observe that the reactions of glycolysis are reversible, but, in reversing, energy is consumed. The energy needed for reforming glycogen from lactic acid comes from the oxidation of a portion of the lactic acid.



Too violent exercise causes such an accumulation of lactic acid that oxidation cannot take place rapidly enough to provide the energy for disposing of it. An "oxygen debt" exists, and as a result the muscles become so fatigued that they cannot respond to stimuli. Resting and deep breathing soon provide extra oxygen for repaying the oxygen debt.

### The Aerobic Phase; Tricarboxylic Acid Cycle:

The lactic acid (or the pyruvic acid from which it is formed), which is not converted to liver glycogen, is metabolized through a series of reactions which produces ultimately carbon dioxide and water, with release of considerable energy. The mechanism by which this is accomplished is known variously as the *Krebs cycle*, after the name of the biochemist who proposed it, the *citric acid cycle*, or the *tricarboxylic acid cycle*. The following diagram pictures this metabolic cycle.

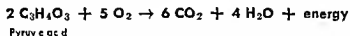


Careful study of this cycle shows that a molecule of acetic acid is consumed in each trip around the cycle. As shown, the acetic acid which enters the cycle proper originates from pyruvic acid, or its reduction product lactic acid. Each chemical change in the cycle is controlled by a specific enzyme; with one exception their names have not been given. In addition there are five transitions which require dehydrogenases, as indicated by  $-2\text{H}$ . The dehydrogenases accept the hydrogen, as indicated, thus oxidizing the

substrate. Eventually, however, the hydrogen is brought into combination with molecular oxygen to form water, and the dehydrogenase is reactivated. Consequently dehydrogenases may be viewed as factors which are "hydrogen carriers."

The union of oxaloacetic acid with acetic acid at the start of the cycle is catalyzed by coenzyme A. This coenzyme brings the acetic acid into an active state (acetyl CoA) for condensation with oxaloacetic acid to form citric acid. It is of interest that pantothenic acid, one of the B vitamins, is incorporated in the structure of coenzyme A.

The over all effect of the tricarboxylic acid cycle is summed up in the following equation



The energy derived from the oxidations, with the exception of the heat, is used to create high energy bonds through the synthesis of ATP from ADP. It is thought that the aerobic phase of carbohydrate metabolism provides fifteen times as much energy as the anaerobic phase.

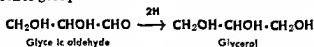
Since it expresses the only way in which nutrients can be completely oxidized, the Krebs cycle can well be considered as a focal point in metabolic processes. We shall find that the intermediary metabolism of fats (lipids) and proteins leads to compounds some of which are identical with those of the cycle. This aids greatly in explaining how the fats, carbohydrates, and proteins are in some respects interrelated in metabolism.

### Conversion of Glucose to Fat

It is generally known that eating much candy and sweets causes one to "put on weight." To fatten such farm animals as cattle and hogs, corn and other grains that contain carbohydrates are used to make up the largest part of their food. In both cases, experience and experiment have shown that animals can change carbohydrates into fats and that carbohydrates may be stored as fat in the body. This ability of the body to synthesize fat from carbohydrates is not very simple from a chemical standpoint and at present the process is far from clear. It is known that a fat is a glyceryl ester of a fatty acid. Therefore, in order to form body fat, both glycerol and fatty acids must be synthesized from the excess carbohydrate.

With the facts already stated pertaining to the conversion of glucose to glyceric aldehyde, it is not difficult to postulate how

glycerol might be formed by the reduction of the aldehyde group to the alcohol group



However, the mechanism of long chain fatty acid formation is somewhat uncertain. Since fatty acids of nutrition always contain an even number of carbon atoms, evidence points to the continued condensation or linking together of two carbon units. The acetic acid of intermediary carbohydrate and fatty acid metabolism represents such a unit. The synthesis of fatty acids may take place via acetyl coenzyme A, although conclusive evidence is lacking.\*

### Carbohydrate Tolerance

We have learned that when carbohydrates are taken into the body a part is oxidized immediately to produce energy, while the remaining portion is stored as glycogen in liver or muscle tissues, or is converted into fat. This capacity of the body to oxidize or store the carbohydrate glucose is called the *carbohydrate tolerance*. Ordinarily, following a meal which contains carbohydrates, the amount of glucose in normal blood rises from about 100 milligrams of sugar per 100 ml of blood (0.1 per cent) to approximately 150 milligrams (0.15 per cent) during the first hour and usually returns to normal by the end of the second hour, because the excess blood sugar is either "burnt" (oxidized) or stored as glycogen or fat. In some cases, the blood sugar may run as high as 180 milligrams (0.18 per cent), nearly double the usual amount. Above this blood sugar level, called the *threshold point* of the kidney, sugar begins to pass into the urine, and gives rise to the condition known as

renal threshold point	170	} to urine
	160	
hyperglycemia	150	} oxidation in the tissues formation of fat and glycogen
	140	
	130	
	120	
	110	
normal level	100	
	90	
	80	
	70	
hypoglycemia	60	
	50	
	40	

BLOOD SUGAR LEVEL (in milligrams per 100 ml)

\* Experiments seem to indicate that thiamine (vitamin B<sub>1</sub>) plays an important role in the synthesis of fat from carbohydrates.

*alimentary glycosuria* It usually requires the consumption of approximately a pound of sugar to produce alimentary glycosuria in a normal person This alimentary glycosuria is not pathological but rather an expression of excessive carbohydrate intake

The ability to utilize carbohydrates, that is, to oxidize or store them, is in part controlled by *insulin*, an internal secretion or hormone of the pancreas Lacking insulin, sugar would simply accumulate in the body An unquenchable thirst for water arises in order to carry this excess sugar from the body Hunger develops, the body steadily loses weight, and there is a lack of muscular energy The inability of the body to secrete an adequate amount of insulin is manifested by a decrease in the carbohydrate tolerance When the blood sugar is above normal, a condition known as *hyperglycemia*, sugar is usually excreted into the urine When hyperglycemia and glycosuria occur after a normal diet the patient very likely has a disease called *diabetes mellitus*, and blood sugar values may be as high as 12 per cent In such a condition the vitality of the patient is low because of the inability to store or burn glucose In chronic diabetes the renal threshold for sugar excretion may be elevated and glycosuria may be absent Consequently more reliance should be placed on an analysis of sugar in the blood rather than on the presence of glucose in the urine It sometimes happens that the patient's threshold point is lowered and glycosuria occurs even when the blood sugar is normal Such a condition of a low sugar threshold is called *renal diabetes* An overdose of insulin commonly brings on the dangerous condition of hypoglycemia (low sugar), often accompanied by convulsions This may be relieved promptly by the administration of sugar

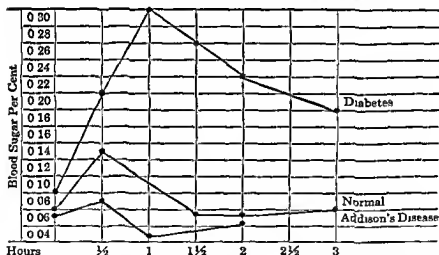
In certain pathological conditions (diabetes, hyperthyroidism, nephritis) the determination of the carbohydrate tolerance has been of the greatest importance in establishing the diagnosis The procedure is as follows A blood sample is obtained from the patient after a 14 hour fast, 50 to 100 Gm of glucose are consumed, blood samples are taken at subsequent intervals of 15 to 30 minutes over a period of two or three hours, and the blood samples are all analyzed for sugar The percentage of blood sugar and the time are plotted as in the diagram on page 514

The maximum height of the curve and the time required to return to normal levels when compared to healthy patients' response shows the severity of the disease In a normal curve the maximum sugar concentration is highest near the end of the first hour but it returns to normal in about two hours A diabetic curve, however,



shows both a greater rise and slower fall. The shape of the curve, drawn by plotting sugar percentages against the time after ingestion of glucose, is of great diagnostic value, especially for the detection of early stages of diabetes; but in using the assimilation curve, it is well to keep in mind that its shape may be altered by such various factors as sugar absorption from the intestines, sugar retention by the liver, and sugar consumption by the tissues. This is particularly significant after prolonged starvation (24 hours or more). The change of glucose into glycogen by the liver is largely dependent upon a group of enzymes, presumably elaborated by the liver cells. Some of the glycogen comes from the absorbed sugar, as has been stated, and some is produced from the glycerol fraction of fats and some from protein. Thus there is always some glycogen in the liver.

#### DETERMINING CARBOHYDRATE TOLERANCE CURVES



The consumption of sugar by the tissues has already been explained. It should be remembered that diabetes mellitus is due primarily to a loss of power on the part of the tissues to utilize sugar. The normal functioning of carbohydrate metabolism in the muscles and other tissues is an important factor in maintaining a healthful body.

Before leaving this discussion we should understand that there are several forms of temporary glycosuria. One condition, alimentary glycosuria following the ingestion of excessive carbohydrate intake, has been mentioned. Another form, stemming from mental strain or great agitation, is called emotional glycosuria, and un-

doubtedly is caused by the production of excessive epinephrine, which is always secreted under emotional excitement. It is at such times that the muscles need an increased fuel supply.

### SELF-TESTING QUESTIONS

- 9 What two changes take place when blood passes through the liver?
- 10 How do you account for a decrease of the glycogen content of the liver?
- 11 What changes are believed to occur during the oxidation of glucose?
- 12 What happens to the lactic acid formed during glucose oxidation?
- 13 What causes muscle contraction?
- 14 To form body fat from glucose what two classes of intermediate substances must be formed?
- 15 What is meant by carbohydrate tolerance and threshold point?
- 16 What factors may alter the shape of an assimilation curve?
- 17 How would you interpret the assimilation curve for sugar?
- 18 What controls the secretion of blood sugar by the liver?

## IV. METABOLISM OF FATS

### Functions of Fats

In the course of digestion of fats, the glycerol and fatty acids formed are absorbed by the epithelial cells of the villi and are recombined in their passage through the intestinal wall to form neutral fats, which are absorbed by the lymphatic vessels. These are drained by the thoracic duct which empties into the venous system at the junction of the left jugular and subclavian veins. In the form of an emulsion, the neutral fats are carried to the cells where they may be (a) oxidized immediately to furnish energy, (b) stored in the tissues as a reserve fuel, and (c) transformed into lipids, fatlike substances that form an essential part of every cell and which are not depleted even during exhaustive starvation. Formerly, the cell membrane was thought to be entirely composed of proteins, but it is now known that fats in combination with proteins (lipoproteins) form very complex substances. These are believed to be an integral and essential part of cell membranes of cellular protoplasm, and of the central nervous system. In this sense fats as well as proteins are tissue builders.

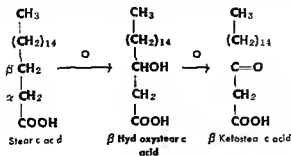
Two very well known lipids are lecithin and cholesterol. *Lecithin*, one of the phospholipids, apparently is an intermediate compound formed in the metabolism of fat. *Cholesterol* is a solid alcohol of high molecular weight and belongs to a group of derived lipids called sterols. It, like lecithin, is connected with fat metabolism in some as yet unexplained manner. In some instances it has a clinical significance. An excess of cholesterol in the blood is suggestive of gall stones, diabetes, pregnancy, and certain renal disorders, especially

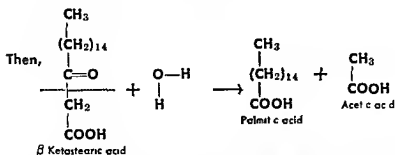
nephrosis In the skin, cholesterol is associated with *ergosterol*, which upon exposure to sunlight or other sources of ultraviolet rays is converted into the antirachitic factor, vitamin D Food products may also be irradiated because they contain ergosterol

### Oxidation of Fats

Although much is yet to be learned about the lipids in cellular structures, we do have considerable information concerning the oxidation of fat in the production of energy Fats must first be split into glycerol and fatty acids before oxidation may take place The splitting is a hydrolytic action probably performed by tissue lipases A glance at the formulas ( $\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$ ) shows that glycerol, like glucose ( $\text{CH}_2\text{OH}-(\text{CHOH})_4-\text{CHO}$ ), has representative alcohol groupings Therefore, the glyceryl fraction of fats acts in a manner similar to glucose, and, upon oxidation produces glyceric aldehyde which is one of the intermediate products in the glycolytic phase of glucose metabolism (p 508) Since glycerol accounts for about 10 per cent of the weight of fat it can be said that this amount of the total fat which is metabolized for energy follows the carbohydrate route of metabolism Such data are important in dietary studies

The fatty acids which are released from fats by hydrolysis are oxidized in stages giving ultimately, in a normal metabolism, carbon dioxide and water as material products The most widely accepted views as to how this takes place are based on Knoop's *theory of beta ( $\beta$ ) oxidation* Here it is supposed that the oxidation first sets in at the beta carbon of the fatty acid chain As learned previously, the beta carbon is the second one after the carboxyl carbon Using *stearic acid* for illustrative purposes the following formulas depict the course of the oxidation





The net result of this sequence of reactions is to produce a molecule of acetic acid and one of palmitic acid, the latter having two less carbon atoms in its chain than the original stearic acid. By a repetition of these reactions palmitic acid will split off a two carbon atom fragment, as acetic acid, and give  $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ . This acid can then give rise to  $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$  and so on until all intermediates have been oxidized to acetic acid. Coenzyme A plays an essential part in these oxidative changes, and actually the acetic acid molecules which are produced appear in activated form as acetyl coenzyme A. Recall that acetyl coenzyme A enters the tricarboxylic acid cycle to be oxidized to carbon dioxide and water, with release of energy.

Notice that the formation of acetic acid, a two carbon atom molecule, as the end product of fatty acid degradation, requires that the original fatty acid have an even number of carbon atoms in its chain. It is interesting to note that this is actually the nature of those fatty acids, which, in the form of glycerides, comprise our natural fats and oils, odd numbered carbon chains are not found.

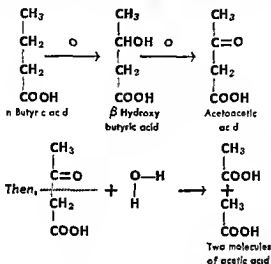
In Knoop's proposal the oxidation follows the usual course, namely secondary alcohol to ketone, followed by splitting to form acids.

Other mechanisms of fatty acid oxidation have been proposed, one of these being the *multiple alternate oxidation theory*. According to this scheme, oxidation of the fatty acid occurs simultaneously on the beta carbon, and on every alternate carbon from this point throughout the length of the chain, to give an acid with multiple ketone groups. Hydrolysis, with splitting, then takes place at the points of oxidation.

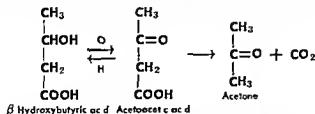
### Incomplete Fat Metabolism

The compounds  $\beta$  hydroxybutyric acid, acetoacetic acid, and acetone are formed in abnormal amounts when fats fail to metabolize properly. To understand how these compounds are produced,

recall that in Knoop's theory of beta oxidation the carbon atoms are removed two at a time as acetic acid from the original fatty acid. Inasmuch as the fatty acids derived from natural foods have an even number of carbon atoms there will be produced ultimately during the oxidation a four carbon atom acid, normal butyric acid. Normally this would oxidize and break down as follows:



In faulty fat metabolism, however,  $\beta$  hydroxybutyric acid, acetoacetic acid, and acetone (the latter formed from acetoacetic acid upon loss of carbon dioxide) accumulate in the tissues and blood. These three compounds are related as follows:



Collectively they are known as the "*acid bodies*" although only two of them are actually acids. Their formation reduces the alkalinity of the blood and tissues and in severe cases the resulting acidosis may lead to coma and even death.

Faulty fat metabolism is associated with an inability to properly metabolize carbohydrates. In severe diabetes, when glucose is not properly stored and oxidized, a form of acidosis commonly called

*ketosis* (formation of acid bodies) occurs. In fact, the serious aspects of diabetes mellitus in the advanced stages can be attributed to the accumulation of acid bodies. The statement that "fats burn in the flame of carbohydrates" colorfully sums up the dependency of proper fat metabolism on a normal carbohydrate metabolism. Apparently an incomplete metabolism of glucose gives insufficient intermediates for the operation of the tricarboxylic acid cycle. Acetic acid cannot be disposed of by the cycle, and therefore the breakdown of fatty acids stops with the formation of four carbon atom products. It is possible that some of the acetic acid which is produced before the four carbon atom stage is reached is used up in synthesis of acid bodies, inasmuch as its normal metabolism is blocked. Acid bodies also appear during prolonged starvation. Here the carbohydrate reserve of the body has been depleted, and energy is realized largely through the extensive catabolism of fatty tissue.

### Ketosis and Antiketosis

The fatty acids, and those amino acids which can metabolize to give "acid bodies," are called *ketogenic* foods (keto = ketosis, genic = formation). Foods such as glucose, glycogen, glycerol, and those amino acids which metabolize as do the carbohydrates, are the *antiketogenic* foods, these favor normal oxidation of the fatty acid fragments, thereby preventing ketosis. When ketosis is due to starvation it is relieved by increasing the carbohydrate diet. In diabetes, ketosis is controlled by correcting the carbohydrate metabolism, often by the use of insulin.

About 58 per cent of the protein food provides amino acids which can be metabolized like carbohydrate. Also, 10 per cent of the fat eaten (glyceryl fraction) metabolizes like glucose. Therefore, in calculating the available carbohydrate in any diet, one always sets the total carbohydrate as equal to (1) 100 per cent of the dietary carbohydrate plus (2) 58 per cent of the dietary protein plus (3) 10 per cent of the dietary fat. It follows then that a diabetic diet should include (a) no more food than is needed for normal energy requirements, (b) as little protein as is required to maintain the nitrogenous equilibrium, a condition during which nitrogen excreted equals the amount taken in by food, and (c) the correct proportion of glucose to fat.

### SELF-TESTING QUESTIONS

- 19 What three things may happen to emulsified fats on reaching the cells?
- 20 What is the clinical significance of an excess of cholesterol?
- 21 In what way is cholesterol important?
- 22 What probably happens to glycerol on oxidation?

23. What are the products of faulty fat metabolism?
24. What is ketosis?
25. What is an antiketogenic substance? Name one.
26. How may ketosis be relieved?
27. How may it be prevented?
28. What are the dangers of fasting?
29. What causes obesity?

## V. METABOLISM OF PROTEINS

### Function of Amino Acids:

In the course of the digestion of proteins, the amino acids formed are absorbed through the intestinal wall, passing unchanged into the blood of the portal vein, and *via* the liver enter the general circulation for distribution to the various tissues of the body. In this circulation, each tissue has the power of selecting the number and kind of amino acids required by that particular tissue. It has been found that there are at least eight amino acids which are essential



Fig. 4—Amino acids, the structural units of proteins. This picture shows some of the scientists who have synthesized from coal and other materials the amino acids that must be included in our diet. How many of these acids are essential in the diet?  
Courtesy, Dow Chemical Co.

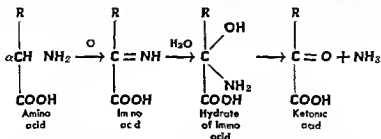
in the diet to maintain the growth and repair of the tissues. These are called "essential" because they cannot be synthesized in the body from other amino acids. Common food substances like eggs, milk, and meat contain a sufficient supply of these amino acids, but some cereal proteins are low in lysine and tryptophan, two of the so-called essential amino acids. Zein, for instance, a protein from corn, contains no tryptophan or lysine. Even gelatin lacks tryptophan and tyrosine, and if either of these two proteins were the sole source of protein in an otherwise adequate diet, the animal would die as certainly as if he were receiving no protein at all.

The absorbed amino acids are available to provide for growth or repair of the protein structure of the cells, those which are not used for this purpose undergo *deamination*, a process involving the splitting off of the nitrogen-containing amino group ( $\text{NH}_2$ ) to form ammonia, while the rest of the molecule, containing only carbon, hydrogen, and oxygen, is either oxidized directly to furnish energy or if sufficient quantities are present, may be converted into glucose and fat.

### Oxidative Deamination

In decided contrast to carbohydrates and fats, *proteins cannot be stored* as protein in the body except in very small amounts. This means that any excess of amino acids not required in tissue construction must be used as fuel or stored as glycogen or fat.

Amino acids formed by the decomposition of the protein molecules apparently are subjected to *oxidative deamination* reactions, principally in the liver and kidney. Oxidation takes place at the alpha carbon to form the corresponding imino acid. This acid probably forms an unstable hydrate, which decomposes to yield a ketonic acid and ammonia as illustrated in the following equation:

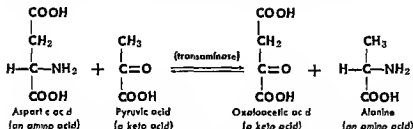


Ammonia split off in the deamination of an amino acid and the carbonic acid of the tissues, by means of a cyclic reaction in the liver, unite to form urea, as will be explained later.



### Transamination

In addition to oxidative deamination, amino acids may also free themselves of amine groups by *transamination*. This requires the presence of an alpha keto acid, to which the amine group is transferred

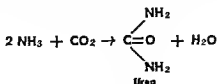


Notice that transamination results in an interchanging of structures. In the example given, aspartic acid transfers its amino group to pyruvic acid, thus becoming oxaloacetic acid, and producing a new amino acid, alanine. Inasmuch as pyruvic acid, an intermediate in carbohydrate metabolism, and aspartic acid, an amino acid in the composition of many proteins, react in this manner, the product alanine is not an "essential amino acid" in the diet. Body requirements for alanine can be met, if necessary, by its formation in the body via transamination.

Reactions of transamination make it possible for the body to synthesize certain needed amino acids from others, providing the necessary keto acids are available. Also, as this discussion has implied, transamination definitely links the metabolism of proteins with that of the carbohydrates. Transamination, and oxidative deamination as well, produce a number of compounds which are also found in the tricarboxylic acid cycle.

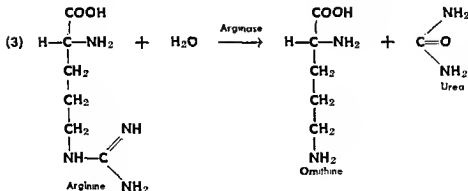
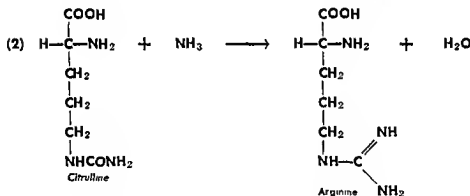
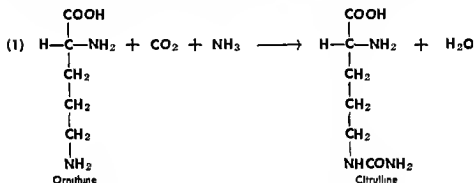
### Urea Formation

The ammonia which is produced in the deamination of amino acids is disposed of largely through conversion into urea, a process which can be summarized as follows:



The synthesis of urea from ammonia and carbon dioxide takes place in the liver. Actually it is a far more complex process than it appears to be as expressed in the equation

Investigators believe that three amino acids are involved in the process: ornithine, citrulline, and arginine. The reactions which make use of these amino acids for the production of urea are indicated by the following equations:



This sequence of changes, which indirectly converts ammonia into urea, is called the *ornithine cycle*, since it begins and terminates with ornithine. After its formation in the liver the urea is carried by the blood to the kidneys and then excreted via the urine. About 80 per cent of protein nitrogen excreted from the body is in the form of urea. This amounts to up to 30 grams of urea for an adult over a 24 hour period.

The digestion and metabolism of those proteins which contain sulfur and phosphorus lead to the production of inorganic acids of these two nonmetals. Some of the ammonia produced in the deamination of the amino acids neutralizes such inorganic acids by converting them into ammonium salts. These are then excreted by way of the urine.

### Nitrogen Balance

Since protein cannot be stored and must be oxidized to yield nitrogenous waste products, it follows that in certain cases of impaired kidney function low protein diets appear to be indicated. However, if the diet is too low in protein and the loss of protein by damaged kidneys is great, or if the protein eaten does not contain the essential amino acids, a negative nitrogen balance results, i. e., more nitrogen is excreted than is present in the food consumed. This may prove more detrimental than the accumulation of nitrogenous wastes in the blood, and the problem must be left to the physician. A positive balance exists when the amount of nitrogen in the consumed protein is greater than that in the excretion, e. g., in growing children. Ordinarily for a normal adult the total nitrogen in the food eaten just equals that excreted into the urine, feces, and perspiration, and a state of nitrogen equilibrium exists.

Before leaving this subject, attention should be called to the effect of a low carbohydrate diet. In fasting, or when an individual eats less to lose weight, the normal supply of carbohydrate may be greatly diminished with the result that the supply of glycogen is soon used up. Consequently, at such times most of the energy comes from body fat, and the acetone bodies appear.

Usually, obesity is the result of overeating or lack of sufficient exercise. There may also be a hereditary factor. It is common knowledge that many thin people eat well and do not take on fat, whereas fat people take on weight. The thin people probably exercise more, eat less high calorie food, and drink less water than do fat people. It is an overlooked fact that unless an individual has

been on a diet for a long time water replaces fat in his tissues. It has been established clinically that faulty functioning of the endocrine glands may be associated with obesity.

The following chart summarizes some of the normal metabolic changes of carbohydrates, fats, and proteins.

### SUMMARY OF NORMAL METABOLIC FOOD CHANGES

Food Carried To Tissues as	Anabolism or Constructive Metabolism	Catabolism or Destructive Metabolism	End Products of Metabolism
Glucose	Glycogen		
	Fat		
		Aldehydes and acids of three carbon atoms	$\rightarrow \text{CO}_2 + \text{H}_2\text{O}$
Fats	Adipose tissue		
	Lipids		
		Fatty acids, by $\beta$ oxidation or by multiple alternate oxidation to	$\rightarrow \text{CO}_2 + \text{H}_2\text{O}$
		Glycerol	$\uparrow$
Amino acids e.g., alanine	Tissue protein		
	Fat		
	Glucose	$\text{NH}_3$	$\rightarrow \text{Urea}$
		Non nitrogenous part of molecule (C, H, O)	$\rightarrow \text{CO}_2 + \text{H}_2\text{O}$

### SELF-TESTING QUESTIONS

- What foods have a sufficient supply of the eight essential amino acids required in a diet?
- What happens to amino acids in absorption?
- What is the meaning of deamination?
- What is transamination?
- Explain what happens in the formation of urea from ammonia
- Where is urea reconverted to ammonia in the body and why?
- What salts are likely to occur in urine?
- How is the total available carbohydrate, from a mixed diet (i.e., containing fat, carbohydrate and protein) calculated, and when is such a calculation of practical value?

## VI. METABOLISM OF INORGANIC SALTS

### Classification of Inorganic (Ash) Elements

We have been studying the metabolism of foods that supply energy and build tissue. In addition to these body requirements, there is a need of other materials that will help regulate body processes and make possible normal metabolism. These are the inorganic or mineral constituents of food substances. By inorganic substances is meant the inorganic salts ( $\text{NaCl}$ ,  $\text{CaHPO}_4$ , etc.) which enter and leave the body as such, as well as other mineral constituents such as the iron in hemoglobin, and the phosphorus and sulfur in protein, which are in combined form with organic matter and which upon oxidation are eliminated as inorganic salts. The inorganic substances with which we are primarily concerned include the elements Na, K, Ca, Mg, Fe, existing mostly as chlo-



Fig. 5—Osteomalacia. Depletion of minerals causes the long bones to become soft, flexible and badly deformed. Besides a calcium and phosphorus deficiency, what other factors may be operating to produce osteomalacia?

rides, phosphates, bicarbonates, and in a lesser amount as iodides and sulfates.

It is convenient to classify the ash elements of the body as an acid group (S, P, Cl) and an alkali group (Na, K, Ca, Mg). A third group, consisting of iron and iodine, is best considered in a separate category as two elements that are found chemically combined in important organic substances such as hemoglobin and thyroxine. A fourth group includes the so called trace elements (F, Cu, Mn, Co, Ni, Al, Si, Bi, etc.), whose functions are not completely understood.

Each inorganic element in the first three groups is needed for growth. Experiments have shown that rats do not grow, and eventually die, if the sodium or the potassium is markedly reduced in their diets. Lack of sufficient calcium and phosphorus also inhibits growth and may produce rickets and osteoporosis of the long bones (Fig. 5). A deficiency of chlorine and magnesium also impairs health. In respect to the "trace elements" it is difficult to say whether the presence of some of them in the body is incidental or essential, although recent experiments have suggested a role for both copper and manganese. It is also interesting to note that, as later explained, all of the mineral elements may be utilized if in the form of simple inorganic salts with the exception of sulfur. Available evidence indicates that the body can utilize only the sulfur of the amino acids, cystine and methionine. Of all of these elements, the ones that are most apt to be deficient in the human diet are calcium, phosphorus, iron and iodine, and because of their known importance in nutrition, special attention is given them as the separate elements are described.

### General Functions of Inorganic Salts

With the exception of the phosphates of calcium and magnesium, all of the inorganic salts are soluble in water and consequently usually occur as ions in the body's fluids wherein they perform special functions. Even though the inorganic salts are almost entirely unoxidizable, or are in the oxidized form, and do not furnish heat or energy, nevertheless their importance to life and health may be appreciated as one considers their chief physiological uses. The general functions of the inorganic salts, briefly stated and later explained in more detail, are these:

- 1 They contribute to the building and repair of tissues
- 2 They influence the contraction of muscles and irritability of nerves
- 3 They help to maintain proper osmotic conditions
- 4 They are largely responsible for the acidity and alkalinity of digestive juices
- 5 They are important factors in the chemical reactions of the body

**INORGANIC SALTS BUILD AND REPAIR TISSUES** The following table shows that carbohydrates, fats, and proteins furnish approxi-

mately 96 per cent of the elements required in human nutrition, and that the remainder must be supplied to the body as inorganic salts, or as organic salts containing some of these elements

### COMPOSITION OF HUMAN BODY

	<i>Approximate Percentage</i>	
Mostly found in carbohydrates fats and proteins	Oxygen	65%
	Carbon	18%
	Hydrogen	10%
	Nitrogen	3%
Mostly found in mineral salts	Calcium	1.5%
	Phosphorus	1.0%
	Potassium	0.35%
	Sulfur	0.25%
	Sodium	0.15%
	Chlorine	0.15%
	Magnesium	0.05%
	Iron	0.004%
	Iodine	0.00004%
	Si and other elements in traces	

Practically all of the elements required for nutrition are found in sufficient quantities in the average well balanced diet. This includes sodium chloride, which is added as seasoning, largely because many foods—especially vegetables—are made more palatable by its use. A good diet includes milk, fruits, vegetables, protein food such as eggs, fish, meat, and cereal products made from whole grains. In periods of growth, during convalescence, and in pregnancy, particular attention must be given to the mineral constituents of foods, for it is well known that minerals are needed to build tissues and the bony structure of the body. During normal adult life, there is less need for minerals, but we should not forget that the body is constantly undergoing change, that nutrients are being used up for repair, and that products are being eliminated from the body as salts in the urine, perspiration, and feces. Consequently, mineral elements must be supplied to maintain normal metabolism. However, a proper diet, especially one that is varied sufficiently, contains all the minerals required to maintain good health.

**Calcium** This element, in the form of calcium phosphate, makes up the larger part of the mineral matter of the *bones* and *teeth*. An inadequate supply of calcium (and phosphorus) in the diet of growing children results in poor skeletal development (osteoid tissue) Any prolonged deficiency of calcium in children results in rickets, a disease which is associated with growth, and is characterized by such types of bone deformity, as bow legs, knock knees, enlarged joints, heading of the ribs, pigeon breast, deformed skull and pelvis However, calcium deficiency is not the sole cause of rickets An adequate supply of phosphorus and vitamin D is essential Growing children require twice as much calcium as that needed by an adult, because of the rapid growth of the skeleton

In pregnancy a continued deficiency may induce softening of the teeth and bones (osteomalacia), but again, calcium deficiency is not the only cause During pregnancy and nursing, the calcium requirements are three times the normal requirement of an adult At such times, a generous supply of milk and leafy vegetables in the diet provides the needed calcium and vitamins This deficiency may also be met by certain inorganic salts of calcium as well as the organic forms of calcium, but adequate vitamins are equally important

The functions of calcium in producing depression of muscular irritability, increasing blood pressure, increasing rate of respiration, in maintaining the proper rhythm of the heart, in forming insoluble calcium paracaseinate (milk clot) from casein, in *clotting the blood* (p 447), and in *contracting the cardiac muscle* (p 191) have already been discussed Much has yet to be learned about the role of calcium in metabolism Milk and cheese are the best sources of calcium for normal requirements

**Phosphorus** This element is so closely related to calcium metabolism that they are usually considered together Phosphorus, like calcium, is associated with *bone growth* and the diseases, such as osteomalacia, resulting from its deficiency It is an essential component of every cell in organic form as in the phospholipids and nucleoproteins In the blood, one form of organic phosphorus is associated with the fat content Lean meats and grains are rich in phosphorus, but unfortunately three fourths of the phosphorus is lost in processing flour Besides being a limiting factor in the development of bone and growth, a phosphorus compound is essential in the clotting of blood Inorganic phosphates are useful as buffer salts for maintaining the acid base balance in the blood,



urine, and probably in the cells. A condition known as osteophagia is due to phosphorus deficiency and is readily cured by the addition of any form of phosphorus to the diet.

**Magnesium** This element, like calcium, occurs largely in the bones, and plays a role in *muscular contraction*. Very little is definitely known concerning its specific functions. Pharmacologically, it is known that magnesium salts depress motor and sensory activity, that oral administration causes catharsis, diuresis, and acidosis, and that animals kept on a magnesium free diet developed severe muscular weakness and died, usually after a series of tonic clonic convulsions.

**Sodium and Potassium** These elements are closely related in their properties and are usually considered together. Both play an important role in the *growth and repair of tissue*. Experiments have shown that growth is not materially affected on a low sodium potassium diet, but in the absence of potassium, growth ceases. According to some authorities the potassium that occurs abundantly in all vegetables tends to modify or increase the elimination of sodium. Low blood potassium has been reported in chronic nephritis and during the post acidotic states of diabetic coma. For other uses of some of these elements in the body refer to page 188.

**Iron** Although making up only 0.004 per cent of the body, iron is one of the most important elements in nutrition, for it is a *constituent of the hemoglobin* of the red corpuscles which carries oxygen to the cells. Iron as a constituent of intracellular pigments, collectively called *cytochrome*, also acts as a catalyst in certain tissue reactions. Hemoglobin functions as an important buffer of the blood, in addition to its prime function of carrying oxygen. A deficiency of iron produces an anemic condition, such as occurs in chlorosis in women. Iron is abundant in green vegetables and in meat. The chemistry of the relation of diet to regeneration of blood in anemia is not yet thoroughly understood. Some beneficial results in producing hemoglobin have been obtained by feeding organs rich in iron such as liver and heart.

According to some authorities, the iron stored in the human liver and that needed for hemoglobin formation is more readily utilized in the presence of small amounts of copper. Experimental evidence furnished from a study on rats showed that small amounts of copper stimulated the utilization of iron for hemoglobin formation. Furthermore, with a complete absence of copper the iron was ineffective in curing the anemia.

**Iodine** As a constituent of thyroxine, the active principle (hormone) of the thyroid gland, iodine is of great importance in maintaining a *normal rate of metabolism*. Iodine is found in nutritional amounts in vegetables, especially those growing near seacoast districts, and in seafoods, particularly in the liver of fish (halibut, cod). When there is a deficiency of iodine, an enlargement of the thyroid gland develops which is known as simple goiter. The use of salt containing sodium iodide has met with considerable success in the treatment of many cases of simple goiter, especially during adolescence.

When there is an overproduction of thyroxin, as in exophthalmic goiter, the use of iodides is contraindicated. This disease is marked by a high basal metabolic rate. However, iodine does lower the basal metabolic rate for a time and may be safely used (only by the physician) in preparing patients for operation (extirpation of part of the thyroid gland).

**'TRACE' ELEMENTS** The remaining mineral constituents (F, Cu, Mn, Zn, Co, Ni, Al, Si, etc.) or so called trace elements, may be grouped together. They are usually found in small amounts, and have very little effect on the acid base balance of the body. Their functions are still largely unknown.

**Copper** As has already been stated, copper is said to favor the conversion of inorganic iron stored in the liver into hemoglobin. Only a trace of it is necessary for this purpose. Copper has been found in all tissues, and is particularly abundant in liver.

**Manganese** This element is widely distributed, and traces of it are claimed to be needed for normal growth and reproduction.

**Fluorine** This element occurs in some natural waters as fluorides. When it is present in water in excess of  $1\frac{1}{2}$  parts per million, it causes a mottling of the skin (brown stained spots) and irregular formation of the teeth of children who drink the water during the period of tooth formation. These dental defects persist throughout life. It has been observed that fluoride in drinking water also has a tendency to decrease the incidence of dental caries. Experiments have indicated that water which contains about one part per million of fluoride does not produce mottling but does have the desirable effect of decreasing dental decay.

**Zinc Aluminum** These and several other trace elements are found in the body, but their role in metabolism and growth is still somewhat obscure.

## Control of the Contraction of Muscles and the Irritability of Nerves

The large muscle of a frog's leg with the sciatic nerve attached has the power of contracting for some time after being removed from the body, providing that the nerve is excited by some appropriate stimulus such as the electric current. During the intervals of stimulation the muscle shortens and thickens, then relaxes, the entire process taking place in a fraction of a second. The response to the stimulus soon becomes more feeble, and in a short time the muscle will cease to contract. However, if the muscle nerve preparation is immersed in Ringer's physiological saline solution (a solution containing the same percentage of sodium chloride and salts of calcium and potassium as occurs in the blood) the muscle will undergo a series of contractions for a longer period of time. It has also been shown that any change in the relative proportions of these salts causes a corresponding change in the response of the nerve and the muscle to stimulation. Furthermore, experimentation has shown that calcium salts produce contraction and that sodium and potassium salts cause relaxation. In a similar way in the body the metallic ions  $\text{Ca}^{++}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$  of the blood play a role in nervous and muscular activities. As a further contribution to these experiments, Ringer found that heart muscle, after removal from the body, could not only be kept beating for hours in this prepared salt solution, but that minute changes in concentration of the  $\text{Ca}^{++}$  and  $\text{K}^{+}$  may affect the activity of the heart. In other words, it is now definitely established that the contraction of muscles and the irritability of nerves are influenced by the concentration of the  $\text{Ca}^{++}$ ,  $\text{Na}^{+}$ , and  $\text{K}^{+}$  ions, and by their relative proportion. As an example of what may happen when the balance between the ions is abnormal, we may take the case of tetany, a disease characterized by twitching or muscular contractions. An examination of blood in such a patient shows low calcium concentration in proportion to the other ions present, a condition which may be relieved by intravenous injection of calcium salts, or the assimilation of foods high in calcium, as milk. The parathyroid glands play an important role in calcium metabolism.

## Maintenance of Osmotic Pressure

It will be remembered (p 101) that *osmotic pressure is the force exerted by molecules or ions in solution*. Osmotic pressure in the living body is manifested through membranes separating tissues

and cells, and water always tends to pass toward the more concentrated solution. Since osmosis is the result of the dissolved particles, the greater the number of dissolved particles the greater will be the osmotic pressure.

If the concentration of salts in the tissues is greater than in the lymph which bathes them, water tends to pass into the tissues, while if the concentration in the cells is less, water passes out of the tissues. The capillary endothelium acts as the membrane. Within a short space of time these differences in osmotic pressure are equalized not merely because of the passage of the water molecules, but also because of the passage of some of the salt ions. It is in this way that nutrients are carried in solution from one tissue to another.

The colloidal material of the cells contributes to the osmotic pressure, but the pressure from the colloidal particles is much less, owing to the relatively small number of colloidal particles as compared to the salt ions. Other factors may also contribute to osmotic pressure. The concentration of water molecules in tissues is determined by the attraction of the water molecules for the dissolved molecules, although in reality this is merely due to a constant tendency to attain osmotic equilibrium.

### Role in Acidity and Alkalinity of Digestive Juices:

In the study of digestion we learned that enzymes are very sensitive to the medium in which they are contained, some functioning best in a weak acid solution (pepsin in gastric juice), some best in a dilute alkaline solution (lipase in pancreatic juice), and some best in neutral solutions (ptyalin in saliva). In all cases, the slightest variation from normal conditions tends to inhibit the action of these enzymes. The acid in the gastric juice is hydrochloric acid. In the intestine the alkali is chiefly sodium bicarbonate. The blood is slightly alkaline and the urine is frequently acid.

### Preservation of Normal Chemical Reactions:

As just stated, any variation in acidity, alkalinity, or neutrality affects certain enzyme reactions. Such a variation may also affect every cell and organ in the body. Acids are constantly being formed as a result of normal metabolism of body tissue and food. Thus from proteins alone we may have carbonic acid formed from carbon, sulfuric acid from sulfur, and phosphoric acid from phos-

phorus The carbonic acid, being very unstable, decomposes readily and may be eliminated as carbon dioxide through the lungs The sulfuric and phosphoric acids, being atable and strong acids, would soon injure the cells, but they always exist as salts

One protective device against too much acid or alkali in the blood is the presence of the buffer salts (including proteins) as explained on pages 185 to 187

Part of the proteins through deamination form ammonia, which also assists in neutralizing acids The ammonium salts of these acids are then excreted in the urine

### SELF-TESTING QUESTIONS

- 38 How are the ash elements classified?
- 39 What elements are most likely to be deficient in common foods?
- 40 State five functions of inorganic salts
- 41 What foods in particular should be included in a sensible diet?
- 42 What are the functions of  $\text{Ca}$ ,  $\text{P}$ ,  $\text{Mg}$ ,  $\text{Na}$ ,  $\text{K}$ ?
- 43 What importance is attached to the presence of copper?
- 44 What happens when there is a deficiency of or an oversupply of, iodine in the body?
- 45 What common foods contain iron?
- 46 How can iron in the liver be more readily available?
- 47 What is Ringer's solution?
- 48 How does  $\text{Ca}^{++}$  on the one hand and  $\text{Na}^+$  and  $\text{K}^+$  on the other affect muscles?
- 49 What factors influence contraction of muscles and irritability of nerves?
- 50 What are the sources of the ions necessary for acid or basic solutions in the body?
- 51 What acids are formed in normal metabolism?
- 52 What happens to them?
- 53 What protective devices prevent too much acid from accumulating in the body?

## VII. METABOLISM OF WATER

### Adaptation of Life to Water.

Life, originating as a single cell in water, first had to develop a mechanism to separate it from its all pervading medium and prevent its dispersion in that medium This mechanism was a covering and protecting membrane through which the cell obtained its food and excreted its waste Life, in the beginning, was dependent on water for everything—food, heat, and mobility As life developed into more complex forms, it moved its habitat from water to wet mud

and then to dry land. These complex life organisms were less dependent on an immediate source of water.

Finally birds and mammals, capable of remaining alive for several days without ingesting any water, evolved. In this period of evolution, the birds and mammals developed a *second mechanism for maintaining a constant internal body temperature*. This came about in adapting the external protective covering, the skin, to prevent the undue loss of water through evaporation. A frog, for instance, removed from its environmental pond and placed into a hot, dry room, dies from desiccation because its skin is unable to control evaporation.

Another mechanism for the maintenance of constant body temperature has come into the possession of the higher forms of life. This is the *ability of the skin to allow the vaporization of large quantities of water when desirable*. This is accomplished through the sweat glands. There is a close relationship between water metabolism and animal heat. A constant body temperature is necessary for normal functioning, even though the production of heat within the body varies. This is accomplished by removing excess heat through direct radiation and conductivity into the air, and by the vaporization of enough water to rid the organisms of the heat not disposed of by the other two methods.

The higher forms of life that have evolved from the primitive unicellular form are still absolutely dependent upon an outside supply of water which serves these important functions: (a) maintains a constant body temperature, (b) keeps the ratio between solids and liquids constant, (c) aids in digestion, and (d) assists in ridding the body of waste matter.

### Water Exchange:

The body's organism is supplied with water from two widely separated sources. On the one hand, it takes in water contained in the solid food and enough other liquid so that the water content of the two added together satisfies its thirst. Another source is the water that is constantly being formed within the body as an end product of chemical reactions. The foodstuffs all contain hydrogen. When they are consumed, most of the hydrogen combines with the oxygen already present in the body, or with the oxygen brought from the outside, to form "metabolic water." The amount of this water depends upon the rate of metabolism. Roughly, 200 to 500 ml. of water are produced in this way every 24 hours.

Water leaves the body through evaporation and excretion. Disregarding the trivial amount in the feces and the amount lost through the lungs, the *kidneys* must have at least 600 to 800 ml daily to carry on their function normally. Much larger quantities are employed by the *heat regulatory mechanism*. The evaporation of water ranges from 800 to 2000 ml in the case of adults who are not laborers. Hard work in a warm climate may necessitate the evaporation of more than five liters of water daily. Even the starving individual lying quietly in a room heated to 70° F (21.1°C) loses some 700 ml of water by evaporation. Since the oxidations going on within the body produce only about one fourth of the amount, the remainder must come from the water normally present in the body. The organism gives up this water reluctantly, and the two mechanisms whose functions are dependent upon it compete with each other for it, as it were. The organism suffers less acutely from renal failure than from a disturbance of its temperature. A manual laborer exposed to tropical heat and unable to obtain water develops hyperthermia in a few hours, and before the day is over will probably collapse with an internal temperature of 106° F (41.1°C) or higher.

Losses of water from the body in excess of the supply, regardless of the cause (vomiting, diarrhea, diabetes, diseases associated with fever), produce an abnormal state that is called *dehydration*. This condition becomes serious if as much as 20 per cent of the body water is rapidly lost. Retention of body water is favored by normal secretion of thyroxine, insulin, and the lecithins. Too much water retention, called *water intoxication*, may also be serious unless sodium chloride is also ingested so that the electrolyte or salt concentration of body fluids is maintained constant. This is the reason why "salt tablets" are taken along with water by individuals who are doing heavy work and perspiring excessively.

In health all of the water that enters the body as food and drink, and whatever arises chemically within the organism, not removed from it by evaporation, from the skin or lungs, is excreted largely in the urine, and a balance between supply and elimination is maintained. But an abnormal organism may increase its water content. The body of the sick man may contain many more liters of water than it did in its former normal state. This acquisition of extra water does not affect the outflow through vaporization. The excess of water is bound to the protoplasm and thus is incapable of passing out through the kidneys. This state in contrast to the

former one is named *hydration*. Clinically this is known as edema or as anasarca.

The following table shows the water exchange for a normal man busily engaged in chemical laboratory work, on a fixed diet and over a period of 72 hours.

### WATER EXCHANGE

<i>Available</i>	<i>Excreted</i>
Intake (diet, water as such) . 5394 ml.	As urine . 1948 ml.
Endogenous (oxidation less hydrated water in body protein or fat that is set free on oxidation)	As feces . 446
1052	As vapor . 3804
—————	—————
6446 ml	6198 ml.

The retention of water by the body was  $6446 - 6198 = 248$  ml

### Water Needs:

The life of the body's organism is not only dependent upon the presence of water, but also upon the proper dilution of substances in solution. For instance, it is well known that the absence of water causes such great concentration of compounds in the tissues and fluids of the body that thirst develops, and eventually leads to pathological disturbances or fatal consequences if not relieved by an intake of water. The desire for water at any time is to bring about a restoration of the normal amount of water required by the body. This will generally amount to two quarts per day and the larger part of this water comes from the foods eaten. The retention and reabsorption of water seem to be associated with a hormone secreted by the posterior lobe of the pituitary gland. Experiment has shown that injury to this portion of the pituitary gland does not allow retention of sufficient water in the tissues or normal reabsorption after filtration through the kidney. Such a condition is prevalent in diabetes insipidus when abnormal volumes of water are voided daily, and large quantities are drunk to satisfy the ever-present thirst of the patient.

Proper dilution of the body's content is of special importance in accelerating salivary, gastric, and intestinal digestion, for, after all, digestion is mainly hydrolysis. From this alone it appears that the drinking of water during meals is a good thing. According to Hawk,



"the drinking of a reasonable volume of water with meals will promote the secretion and activity of the digestive juices, and the digestion and absorption of the ingested food, and will retard the growth of intestinal bacteria and lessen the extent of the putrefying processes in the intestine " Cold or hot beverages produce only a momentary change in stomach temperature

### SELF-TESTING QUESTIONS

- 54 What are the mechanisms for the elimination of water from the body?
- 55 How is the body temperature kept normal?
- 56 What two functions of the body regulate the amount of water leaving the body?
- 57 What does an increased water content in an animal organism depend upon?
- 58 What causes a desire for water?
- 59 What amount of water is normally required per day?
- 60 Drinking water with meals performs what functions?

### SUGGESTED ACTIVITIES

#### I THOUGHT PROVOKING QUESTIONS

- 1 How is a basal metabolism measurement of practical value in estimating the food needs of the body?
- 2 What disadvantages would a purely vegetable diet have for a person in normal health?
- 3 Under what conditions may sugar be found in the urine?
- 4 Since both carbohydrates and proteins can be changed to fats in the body why are fats an essential part of the diet?
- 5 What is meant by a positive and negative nitrogen balance?
- 6 Is the use of an iodide in common table salt beneficial? Explain
- 7 In what way would basal metabolism measurements be of practical value in large institutions? Explain
- 8 What is your opinion of the value of drinking water which contains sulfur compounds as a supply of sulfur for body needs?
- 9 What factors should be considered for rapid loss of excess weight?
- 10 Why is goiter more prevalent in inland cities than in seacoast cities? Explain
- 11 Are iron compounds in mineral waters valuable for good health?
- 12 What happens to the nitrogen content of the amino acids in the process of metabolism?
- 13 Why is it that only infants develop rickets?
- 14 How would you expect the B M R to be affected by fevers? by certain drugs?

**II VOCABULARY TESTING OF NEW TERMS**

metabolism	carbohydrate tolerance	transamination
basal metabolic rate	threshold point	glycolysis
catabolism	renal diabetes	ornithine cycle
anabolism	ketogenic	tricarboxylic acid cycle
deamination	antiketogenic	nitrogen balance

**III TOPICS FOR ORAL OR WRITTEN REPORTS**

- 1 Variability in the Metabolism of Women
- 2 Influence of Food on Metabolism Specific Dynamic Action
- 3 Physical Regulation of Heat in the Body
- 4 Hormones in Metabolism

**LABORATORY CHEMISTRY**

Laboratory exercises for this chapter will be found on page 756

## HORMONES

## CHAPTER OUTLINE

- |  |   |
|--|---|
| <p><b>I. GENERAL FUNCTIONS OF THE HORMONES</b></p> <p><b>II THE HORMONE OF THE PANCREAS</b></p> <p>(a) Insulin</p> <p>(b) The chemical nature of insulin</p> <p>(c) The role of insulin in carbohydrate metabolism</p> <p>(d) Insulin derivatives</p> <p><b>III, THYROID AND PARATHYROID</b></p> <p>(a) The thyroid hormone</p> <p>(b) The parathyroid hormone</p> <p><b>IV. HORMONES OF THE ADRENAL GLANDS</b></p> <p>(a) Epinephrine, the hormone of the adrenal medulla</p> <p>(b) Hormones of the adrenal cortex</p> <p><b>V. THE ENDOCRINE ACTIVITY OF THE GONADS</b></p> <p>(a) The testicular hormone</p> | <p>(b) The female sex cycle</p> <p>(c) The estrogens</p> <p>(d) The corpus luteum hormone</p> <p><b>VI THE PITUITARY GLAND AND ITS HORMONES</b></p> <p>(a) The growth hormone</p> <p>(b) Gonadotropic hormones of the anterior pituitary</p> <p>(c) The lactogenic hormone</p> <p>(d) The thyrotropic hormone</p> <p>(e) The adrenocorticotrophic hormone (ACTH)</p> <p>(f) The diabetogenic hormone</p> <p>(g) The posterior pituitary</p> <p><b>VII THE GASTROINTESTINAL HORMONES</b></p> <p>(a) Gastrin</p> <p>(b) Secretin</p> <p>(c) Cholecystokinin</p> <p>(d) Enterogastrone</p> <p>(e) Enterocrinin</p> |
|--|---|

## I. GENERAL FUNCTIONS OF THE HORMONES

It has been pointed out in previous chapters that certain glands of the body produce external secretions which are carried away from the glands by means of ducts. Examples of this type include the salivary glands, the pancreas, and the liver. There are, in addition to this type of gland, others which do not possess ducts but whose secretions appear to be carried to other parts of the body by the blood stream. These latter glands are known as the ductless glands or the glands of internal secretion. They are also called endocrine organs (Fig. 1). The active chemical compounds that are produced by the endocrine organs are known as hormones. These substances act as chemical messengers and regulate processes of a varied character throughout the body. All activities within the body are under the control of either the nervous system or hormones or a combination of the two.

Dysfunctions of the endocrine glands which result in excessive or inadequate quantities of hormones within the body produce severe diseases. To be able to understand the medical and nursing

problems that result from endocrine disturbances, it is necessary to have a thorough knowledge of the chemistry and physiology of the hormones. The hormones will be discussed with regard to the endocrine organs which are responsible for their formation.

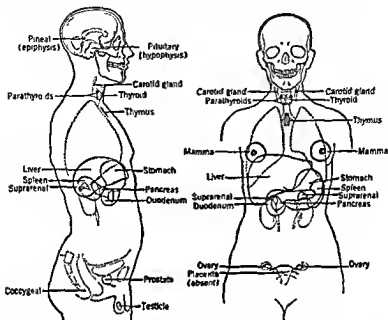


Fig. 1—Endocrine Organs. Diagrammatic chart showing the location of the various endocrine organs.

## II. THE HORMONE OF THE PANCREAS

### Insulin:

The pancreas is an organ of both external and internal secretion. The external secretion is the pancreatic juice, which plays an important role in digestion. The pancreas is also responsible for the formation of insulin, a hormone which is necessary for the proper metabolism of carbohydrates. Removal of the pancreas from an experimental animal produces a condition essentially identical with diabetes mellitus, characterized by increased blood sugar concentrations, glycosuria, acidosis, and eventually coma and death. In 1921, Banting and Best successfully prepared an extract of the pancreas which, when administered to a diabetic animal, reversed the signs and symptoms of the disease. The active principle of this extract was given the name insulin since evidence indicated that

it was derived from that portion of the pancreas known as the islands of Langerhans. Since the discovery of this hormone much has been learned of its chemistry and physiological action.

### **Chemical Nature of Insulin**

Insulin is a protein which has been prepared in crystalline form. All of the insulin used in the treatment of human diabetes is obtained by extraction from pancreas and its production is a by-product of the meat industry. From all the evidence available, it appears that insulin prepared from the pancreas of different animals is chemically identical. Because of its protein character, insulin cannot be administered by mouth since the protein would be hydrolyzed by the enzymes of the gastrointestinal secretions. There are no satisfactory chemical methods for the determination of insulin, so that measurements must be conducted by biological assay. A unit of insulin is defined as one third that quantity which when administered to a rabbit, will produce convulsions due to excessive lowering of the blood sugar. Pure crystalline insulin has an activity of 22 units per milligram.

### **Role of Insulin in Carbohydrate Metabolism**

Although insulin plays a vital role in carbohydrate metabolism, the exact mechanism of its action is not yet understood. In the absence of adequate amounts of insulin, glycogen is not stored in the liver, excess quantities of glucose accumulate in the blood, considerable amounts of this sugar are excreted in the urine and the oxidation of glucose in the muscles is at least partially inhibited. In addition, the deranged metabolism of glucose causes a simultaneous disturbance of fat metabolism manifested principally by excessive production of ketone bodies. Two of these ketone bodies are acidic compounds that cause acidosis. Many of the symptoms of diabetic coma can be related directly to this acidosis. Administration of adequate quantities of insulin to a diabetic patient decreases the blood sugar, eliminates glycosuria, promotes storage of liver glycogen and restores normal carbohydrate oxidation in the muscle. With the return of carbohydrate metabolism to normal, the excessive ketone body formation disappears. Administration of too much insulin to a diabetic causes the blood sugar to be lowered to a level that is not compatible with normal function of the brain and as a result a shock-like state accompanied by convulsions follows. This condition is called insulin shock. The appearance of

a patient who is in a diabetic coma due to an inadequacy of insulin is many times quite similar to that of a patient suffering from insulin shock. Obviously it is very important to be able to distinguish between these two states. This can be readily accomplished by a determination of the blood sugar, a low blood sugar concentration (hypoglycemia) indicates that the patient is in a state of insulin shock, whereas an elevated blood sugar concentration (hyperglycemia) indicates diabetic coma. Administration of insulin in quantities sufficient to produce insulin shock often has a beneficial effect on certain mental disorders such as schizophrenia or dementia praecox.

Originally it was believed that all cases of diabetes were due to inadequate production of insulin by the pancreas. However, it has been observed in experimental animals that the removal of the anterior pituitary gland will relieve the symptoms of diabetes in an animal suffering from this disease as a result of the removal of the pancreas. Also it has been noted that the administration of extracts of the anterior pituitary gland will produce symptoms of diabetes in a normal animal with an intact pancreas. This has led to the concept that there is a hormone produced by the anterior pituitary gland which antagonizes insulin and that a diabetic state may result from an imbalance of these two hormones, either a deficiency of insulin or an excess of the diabetogenic hormone of the anterior pituitary gland. Recently, patients with carcinoma of the pancreas have had practically the whole organ removed surgically. The diabetes that develops in such patients is not as severe as that observed in many diabetics.

### Insulin Derivatives

Since insulin cannot be given by mouth, it must be administered by injections—usually hypodermically. The frequency of administration and the quantity given depend upon the severity of the diabetic state. In most cases, however, with normal insulin, several injections are required each day since the insulin is quickly absorbed from the site of injection, manifests its effect rapidly, and within a relatively short time apparently disappears. Two derivatives have been prepared which are sufficiently slowly absorbed from the site of injection so that only one injection per day is required. Not only is this of much less inconvenience to the patient, but also it makes available to the body a steadier, more even supply of insulin throughout the 24 hour interval. One of these compounds (protamine zinc insulin) is a combination of insulin, zinc, and a

basic protein known as protamine, the other (globin insulin) is a combination of insulin and the protein portion of hemoglobin which is called globin

It has been noted that the injection of an organic compound, alloxan, produces a selective destruction of the cells within the pancreas which synthesize insulin. This drug affords a convenient means of producing experimental diabetes which is very necessary for a better understanding of this disease. It should be recognized that although insulin provides an adequate treatment for diabetes, it does not cure the condition and practically nothing is known regarding the cause of diabetes in man. At the present time there is no evidence that alloxan is an etiological agent in human diabetes even though its chemical structure is closely related to certain important compounds within the body.

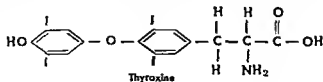
### SELF-TESTING QUESTIONS

- 1 How can experimental diabetes be produced in an animal?
- 2 What is the chemical nature of insulin?
- 3 What are the advantages of protamine insulin or globin insulin?
- 4 What effect does the administration of insulin have on blood sugar?
- 5 How can insulin shock be distinguished from diabetic coma?

## III. THYROID AND PARATHYROIDS

### The Thyroid Hormone

The thyroid gland is a small organ located in the lower part of the neck and consists of lobes on either side of the trachea. An insight into the action of this gland can readily be obtained by observing the disturbances of normal body activity that result from dysfunction of this organ. It has been demonstrated that the action of the thyroid is mediated through a hormone which it produces. An outstanding characteristic of the thyroid hormone is that it contains relatively large quantities of the element iodine. Kendall first succeeded in isolating an active principle from the thyroid gland and found it to be an iodine-containing amino acid which was called thyroxine. The chemical structure of thyroxine is indicated below.



Thyroxine possesses all of the physiological and pharmacological activity that can be attributed to thyroid substance. A second iodine-containing amino acid, diiodotyrosine, has been isolated from the thyroid gland but it is not biologically active. There is evidence to indicate that within the body thyroxine is conjugated as a part of a protein molecule called thyroglobulin, and in reality thyroglobulin is the true hormone of the thyroid gland. However, it appears that when thyroxine is administered it is readily con-

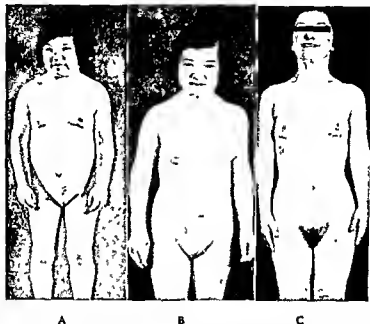


Fig. 2—Cretin, age eighteen. Irregularly and inadequately treated; onset in infancy; no palpable thyroid; presumably congenital athyreosis. A, before institution of adequate therapy. B, after three months of treatment. C, after one year of treatment. Hurxthal, L. M., and Musulin, N.: *Am J. Med* 156 (July) 1946.

verted into thyroglobulin with the result that thyroxine and thyroglobulin have essentially the same physiological and pharmacological effects. In the treatment of hypothyroid states, where it is desirable to supply additional thyroid hormone to the body, pure thyroxine may be either supplied by mouth or injected, or whole dried thyroid gland may be ingested by mouth.

One of the principal activities of the thyroid gland is the regulation of the basal metabolism of the body. One might consider



the body composed of a tremendous number of cells each of which could be compared to a tiny motor which is continuously using fuel and producing heat regardless of whether any actual work is being done. This "idling" activity of the body cells is the basal metabolism. The rate of idling speed of each tiny motor is dependent upon the amount of thyroid hormone circulating in the body. An excess of the hormone causes the motor to race, whereas a diminished amount results in a reduction of the idling speed or basal metabolism. Dysfunction of the thyroid may manifest itself by either an increase or a decrease in the output of the thyroid hormone. One of the most convenient means of determining hypo- or hyperthyroid states is the measurement of the basal metabolism which is usually expressed as a plus or minus percentage of the deviation from normal. For instance, a figure for basal metabolic rate of  $-32$  means that the metabolism is 32 per cent less than normal, which would be indicative of a hypothyroid state; and a figure of  $+65$  means that the metabolism is 65 per cent greater than normal and indicates a state of hyperthyroidism. Most authorities grant a 20 to 30 point range as normal.

Inadequacy of thyroid hormone in a growing child results in a retardation of mental and physical development. This condition is called cretinism and the patient is referred to as a cretin. Fig. 2



Fig 3—Myxedema This severe form of hypothyroidism in adults is characterized by coarse hair, decreased activity (mental and physical). How can this condition be benefited? Courtesy, Dr R A Shipley

shows a typical cretin both before and after treatment with thyroid hormone. If thyroid inadequacy develops in an adult, a characteristic puffiness of the skin results. This condition is spoken of as myxedema and can be relieved by the administration of either thyroxine or desiccated thyroid (Fig 3). Simple goiter is an enlargement of the thyroid gland that occurs in growing children as a result of inadequate intake of iodine. Studies where iodine



Fig 4—Adenomas of the Thyroid and the removed specimens. Notice the huge advanced growth of the tumors and the weak condition of the patient who did not have sufficient strength to survive long after the operation. What would have happened if this patient had seen a competent surgeon earlier in the stage of this disease? Courtesy University Hospitals Cleveland, Ohio.

was added to drinking water or to table salt have indicated that simple goiter can be eliminated by sufficient iodine intake. Although simple goiter in itself does not appear to be a serious condition, certain evidence suggests that subsequent severe thyroid disorders are more likely to occur in persons with simple goiter (Fig. 4). Acute restriction of iodine intake during growth may result in cretinism.

Hyperthyroidism occurs in patients suffering from Graves' disease which is also called exophthalmic goiter. This term arises from the fact that such patients have exophthalmos, a protrusion of the eyeballs. In such cases the basal metabolism is increased from 30 per cent to 100 per cent above normal. Formerly, conventional treatment involved the removal of a portion of the thyroid (partial thyroidectomy). A series of drugs has been discovered which selectively decrease thyroid activity and thus provide a medical means for the control of exophthalmic goiter. The most extensively used of these drugs is propyl thiouracil. This compound is a sulfur derivative of the pyrimidines, a type of compound found in the nucleoproteins of the body. The administration of propyl thiouracil causes a decrease in the basal metabolism to normal, exophthalmos may disappear, and the general condition of the patient is markedly improved. Two other chemical compounds with a comparable effect on thyroid activity are thiourea and thiouracil. Excessive administration of any of these drugs will produce a hypothyroid state.

Treatment of hyperthyroidism is also carried out by administration of radioactive iodine. In thyrotoxic patients who have not recently received iodine, 50 to 90 per cent of the radioactive material is taken up by the thyroid gland and the rest is rapidly excreted. The radiation emanating from the radioactive iodine depresses the activity of the thyroid.

### The Parathyroid Hormone

The parathyroids are four tiny glands which are usually imbedded in the thyroid tissue. Complete removal of these glands leads to deficiency symptoms and subsequent death. Evidence has been obtained to show that these glands elaborate a hormone which plays an important role in the regulation of the calcium concentration in the serum. With an excess of the hormone, serum calcium is elevated to as much as twice the normal level of 10 mg /

100 ml, and with inadequate quantities of the hormone the serum calcium may fall to one half the normal concentration

Extracts of the parathyroid glands have been made which contain the parathyroid hormone. The active principle is called parathormone or parathyrin. It possesses the properties of a protein and has not been successfully isolated as a pure compound.

Dysfunction of the parathyroids may manifest itself either by increased production of the hormone or by inadequate output. Most commonly, hyperparathyroidism results from adenoma or hyperplasia. This brings about a mobilization of bone calcium and a thinning of the skeleton. The serum calcium level is increased and there is also an elevated urinary calcium excretion. Very frequently, some of the excess serum calcium is deposited in the kidney, causing a chronic nephritis and renal failure. Treatment for hyperparathyroidism entails surgical removal of a portion of the enlarged parathyroid tissue. Hypoparathyroidism may arise from accidental removal of the parathyroids during thyroidectomy. In this condition the serum calcium level is decreased and a state of tetany results. This is due to the fact that the calcium concentration of the body fluid has an important regulating action on the irritability of the neuromuscular system. With inadequate calcium, the irritability increases and tonic spasms of single muscles occur, or occasionally there may be generalized convulsions. It should be noted that tetany may also result from marked lowering of the serum calcium because of nutritional deficiency of calcium. This condition is often observed in infants and is spoken of as spasmophilia. Hypoparathyroid tetany can be controlled by the administration of parathormone. Temporary relief can also be obtained by the administration of large quantities of calcium salts. It has been found that certain irradiated ergosterols, particularly the substance called dihydrotachysterol, have an action similar to parathyroid hormone and increase serum calcium levels.

### SELF-TESTING QUESTIONS

- 6 What type of compound is thyroxine?
- 7 What element is present in thyroxine that does not occur in most organic compounds?
- 8 What disease results from excessive secretion of thyroid hormone?
- 9 What is myxedema?
- 10 What is cretinism?
- 11 What is the relation of basal metabolism to thyroid activity?

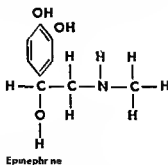
- 12 What nutritional deficiency causes simple goiter?
- 13 What is the action of propyl thiouracil?
- 14 What is the chemical nature of the parathyroid hormone?
- 15 What effect does the parathyroid hormone have on serum calcium concentration?

#### IV. HORMONES OF THE ADRENAL GLANDS

The two adrenal glands, which are sometimes called the suprarenal glands, are situated one at the top of each kidney. Examination of the histological structure of these glands indicates that there are two distinct parts which are called the medulla and the cortex. Actually these two portions of the glands have an entirely different embryological origin and a distinct independent function. The medulla, or inner part of the gland, arises from the sympathetic nervous system and produces a hormone (epinephrine) which has a specific effect on the nerve endings of the sympathetic system. The outer part of the adrenal is called the cortex and is of an epithelial embryological origin. The cortex produces a series of steroid hormones which play an important role in regulating a number of body functions which will be discussed.

##### Epinephrine, the Hormone of the Adrenal Medulla

This hormone was first isolated in 1901 and has since been chemically identified and synthesized. Its chemical structure is shown below and it will be seen that it has a structure which bears a resemblance to the amino acid, tyrosine.



There has been a considerable amount of misunderstanding among physiologists regarding the contribution that the adrenal medulla makes to the economy of the organism. For instance, it

is possible to remove the adrenal medulla without any detrimental effects. However, this does not prove that this portion of the gland has no function. One group of investigators headed by Cannon has provided evidence to indicate that the principal activity of the adrenal medulla is to enable the body to cope with emergencies more readily. Under these circumstances, nervous stimulation of the medulla causes epinephrine to be liberated into the blood stream. The presence of this hormone in the blood results in a dilatation of the bronchioles, an increase in blood pressure, an increase in blood sugar because of the conversion of liver glycogen into glucose which is picked up by the blood, and a decrease in blood coagulation time. Thus in times of stress more oxygen is provided for the blood and tissues (bronchiolar dilatation), more fuel is available for metabolic reactions (increased blood sugar), a better supply of blood is afforded to the tissues (increased blood pressure), and the tendency to bleed as a result of injury is decreased (shortened coagulation time).

Epinephrine has a powerful vasoconstrictor action and for this reason it is used rather extensively in medicine and dentistry to accomplish reduced blood flow in localized areas of the body. For instance, where a local anesthetic is being employed, the anesthetic effect is prolonged by the addition of epinephrine to the injected solution. This causes a reduced blood flow to the area and the anesthetic is not as readily carried away by the blood stream. Similarly, it is possible to decrease bleeding, such as might occur after the extraction of a tooth by the local injection of epinephrine which constricts the blood vessels and abolishes the hemorrhage. Epinephrine given by injection is also useful in the treatment of asthma by reason of its ability to dilate the bronchioles. Epinephrine is likewise employed to resuscitate the heart in cases where the heart has stopped beating. In this instance, it is injected directly into the heart muscle.

### Hormones of the Adrenal Cortex

The adrenal cortex has a much more vital function than does the adrenal medulla, since the removal of this portion of the gland from most animals results in death in a very short time. Similarly, diseases which affect the adrenal cortex are of a very grave nature and unless properly treated are fatal. It has been found that if extracts of the adrenal cortex are administered to adrenalectomized animals, they can be maintained in good condition. The extracts

of the adrenal cortex supply hormones which are normally provided by the gland. The nature of the functions which are regulated by the adrenal cortical hormones can best be appreciated by considering the disturbances that occur in adrenalectomized animals or patients suffering from adrenal cortical insufficiency (Addison's disease). The chief symptoms in such animals or patients are:

(1) A disturbance of water and electrolyte balance which manifests itself by dehydration, a concentrating of the blood, a decrease in the sodium content of the serum and an increase of the potassium content.

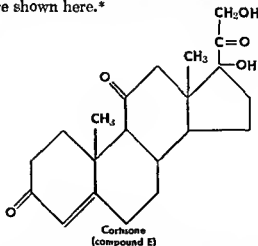
(2) A disturbance of carbohydrate metabolism which is manifested by a hypoglycemia (lowered blood sugar) and a decrease in liver glycogen

(3) A decrease in kidney function which results in the accumulation of urea and other waste products in the blood.

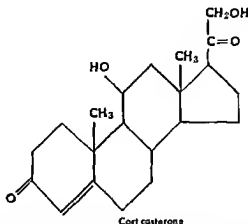
(4) A generalized muscular weakness and a lessened resistance to cold and shock, and other stress reactions

(5) In patients with Addison's disease there is also a bronzing of the skin which gives such patients a characteristic appearance.

Chemical study of adrenal cortical extracts has resulted in the isolation of several steroid compounds. These all possess the cyclopentanophenanthrene nucleus and differ only in the groups that are substituted on this polycyclic structure. The chemical formulas of cortisone and corticosterone, two of the most active of these compounds, are shown here.\*



\* In complex structural formulas of this type the hexagon is not an aromatic (benzene ring) configuration, unless the alternate double and single bonds are shown. It is understood that where lines meet a carbon atom is present, with sufficient attached hydrogens to make it tetravalent. Note that cortisone has no aromatic character.



Cortisone has recently been synthesized and is at present widely used in treating a variety of diseases. Corticosterone is a very active adrenal hormone but is not at present available for medical use. A third steroid called desoxycorticosterone has never been recognized as a chemical component of the adrenal gland but has been synthesized in the chemical laboratory and has a definite effect in regulating or influencing body functions that are under the control of the adrenal cortex. Cortisone primarily influences carbohydrate, fat and protein metabolism and gives either man or animals a remarkable ability to cope with stress reactions. It has a lesser effect in regulating water and electrolyte balance but this function is markedly influenced by desoxycorticosterone.

During the past few years, with the increase in knowledge of the function of the adrenal cortex and with the synthesis of cortisone and desoxycorticosterone, the outlook of a patient with Addison's disease has markedly improved. The simple expedient of restricting the intake of potassium and increasing the intake of sodium chloride is of immense value to the general condition of such patients. It is also possible to implant pellets of desoxycorticosterone under the skin. These very slowly dissolve over a period of several months and afford a constant supply of the factor which regulates water and electrolyte balance. Cortisone may be administered to overcome the effects of any stress reactions (e.g., infections) which may be encountered.

Cortisone also induces prompt remission of acute signs and symptoms of rheumatoid arthritis, including swelling, local redness and tenderness. It has been used with success in all of the other so-called collagen group of diseases (which includes disseminated



lupus erythematosus, periarteritis nodosa, dermatomyositis and scleroderma) The compound is a potent metabolic agent whose administration must be carefully controlled Continued administration produces disturbances in carbohydrate metabolism and development of Cushing's syndrome (See Fig 9, p 568) Effects comparable to those obtained with cortisone can be obtained by the administration of the adrenocorticotrophic hormone (ACTH) of the anterior pituitary This hormone is also widely used in medical practice ACTH acts on the adrenal gland and stimulates the gland to release cortisone and other adrenal cortical hormones With an intact adrenal cortex, the action of cortisone and ACTH are comparable In the absence of a functional adrenal cortex, ACTH has little effect

The adrenal cortex also exerts an effect on sex Tumors of the adrenal cortex in women result in an "adrenal virilism" which manifests itself by the development of secondary male sex characteristics including growth of a beard, lowering of the pitch of the voice, and a repression of female sex characteristics Tumors of the adrenal cortex in males result in a less well defined syndrome In some instances there is an increase in male characteristics, whereas in other cases, there may be a tendency toward feminization with genital atrophy, enlargement of the breasts, and an elevation of the pitch of the voice

### SELF-TESTING QUESTIONS

- 16 Describe the action of epinephrine
- 17 Why is epinephrine useful as a local hemostatic agent?
- 18 What are the effects of disease or removal of the adrenal cortex?
- 19 What is corticosterone?
- 20 What is desoxycorticosterone?

## V THE ENDOCRINE ACTIVITY OF THE GONADS

The gonads (testicles or ovaries) have two types of activity One of these is the formation of spermatozoa or ova and the other, the production of hormones The nature and function of these hormones will be discussed in detail in the following paragraphs

### The Testicular Hormone

The testes elaborate a type of hormone which regulates a number of body functions in the male It is responsible for the descent of the testicles the development of the accessory reproductive organs (epididymis, vas, prostate, seminal vesicles, and penis), the

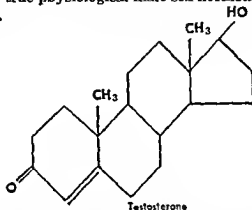
maintenance of spermatogenesis, the development of secondary male characteristics (male voice, male pattern of facial and body hair distribution, male type of skeletal muscular development), and it stimulates libido. Since there are several compounds which possess male hormone activity, they are collectively referred to as the androgens.



Fig. 5—The influence of the administration of testosterone propionate to 24 day old white leghorn chicks. Note the tremendous stimulation of the comb caused by the androgenic hormone. Courtesy Dr. Ralph I. Dorfman.

The androgens can be assayed by injecting them into a capon (castrated rooster) and measuring the amount of comb growth produced. This is possible since the comb growth in the rooster is controlled by male hormone and in the capon there is very little comb growth.

Chemically the androgens are all of a steroid nature. The most potent of them is testosterone which can be obtained from the testis by extraction with a lipid solvent. This compound is believed to be the true physiological male sex hormone. Its structure is shown below.



A second androgen (androsterone) is present in male urine. It has a structure similar to testosterone but the physiological activity is considerably less as measured by comb growth assays in capons (Fig. 5) or as indicated by clinical effects when administered to eunuchs. Testosterone has a definite clinical usefulness in cases where the testes are absent or hypofunctional. Eunuchs, for instance, have a feminine type of body build, slight growth of facial hair, a high-pitched voice, and no sexual urge. Administration of testosterone produces marked changes in body contours, growth of a beard, a lowering of the voice to the male range, an acquirement of sexual desire, and an increase in vigor and sense of well being.

### The Female Sex Cycle:

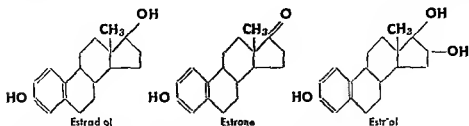
There are two important types of female sex hormones, both of which originate in the ovaries. These hormones are responsible for the development of secondary female sex characteristics, and also regulate the menstrual cycle and play an important role in pregnancy.

The action of the female sex hormones can better be understood following a brief description of the female reproductive system

which includes the ovaries, the oviducts, the uterus, the vagina, and external genitalia. The ovaries are small bean shaped bodies which are responsible for the production of female egg cells (ova). At periodic intervals, an ovum is discharged into the oviduct (fallopian tube) and passes from there into the uterus. If, as a result of asexual intercourse, spermatozoa are present in the uterus, the ovum may be fertilized, if this takes place, the fertilized ovum becomes implanted in the wall of the uterus and develops into an embryo. During the period from puberty to the menopause the ovaries and uterus undergo continuous complex changes. Present in the outer wall of the ovary are large numbers of immature graafian follicles containing ova. During each menstrual cycle, one of these follicles enlarges and secretes increased quantities of estrogens, one of the two groups of female sex hormones. Approximately on the 14th day of each menstrual cycle in the human, the enlarged follicle reaches maturity and discharges an ovum. At the point where the follicle ruptures, the cells undergo a change (luteinization) and the resulting structure is called the corpus luteum. This corpus luteum is responsible for the production of progestational hormones, the second of the two groups of female sex hormones. If pregnancy does not occur, the corpus luteum undergoes atrophy approximately at the time of menstruation, whereas, if the ovum is fertilized, the corpus luteum persists throughout pregnancy. During the time the graafian follicle in the ovary is developing, the endometrium (the lining of the uterus) undergoes proliferation, which may be thought of as a type of development rendering the endometrium capable of receiving a fertilized ovum. If the ovum is not fertilized, the endometrium undergoes further changes and at the time of menstruation, the inside surface of the endometrium sloughs off leaving many exposed blood vessels which account for the menstrual bleeding. In most animals, menstruation does not occur and the female is receptive to sexual intercourse only at certain periods.

### The Estrogens

There are several substances of similar chemical nature which have a specific physiological action and these substances are collectively referred to as the estrogens. They are produced by the ovaries as a result of pituitary stimulation, circulate in the blood, may be metabolized or chemically altered, and are excreted in the urine. The following formulae show the structures of the three most important estrogens



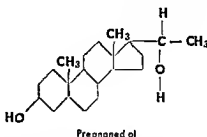
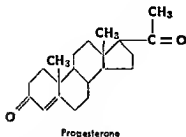
It is believed that estradiol, which is the most potent of the three compounds, is the true hormone and that estrone and estr'ol are products of the metabolism of estradiol. Estradiol is produced by the follicle cells of the ovary and is secreted in increased amounts during the maturation of a graafian follicle. This increased amount of estrogen causes the development of the endometrium following menstruation and produces a type of structure which makes the uterine wall receptive to the implantation of a fertilized ovum. Estrogens also are responsible for the development or accentuation of secondary female sex characteristics (body contour, hair distribution, development of genitalia, etc.). In most animals, they induce estrus which is the period of "heat" in which the female is receptive to sexual intercourse.

During recent years, estrogens have been extensively employed in the clinical treatment of ovarian insufficiency. They are also useful in the alleviation of severe menopausal symptoms that sometimes occur in middle aged women. A group of synthetic organic compounds which have estrogenic activity has also been developed for the same purpose. The principal one of these substances is diethylstilbestrol. These synthetic compounds are much less expensive than natural estrogens and have the added advantage that they can be administered orally whereas most natural estrogen preparations must be injected.

### The Corpus Luteum Hormone:

The hormone of the corpus luteum (progesterone) has been isolated as a pure chemical compound and its chemical structure determined.

It will be seen that it possesses the basic steroid nucleus but close scrutiny indicates that there are differences between the estrogens, androgens, and progesterone. The second substance pictured is pregnanediol which is the metabolized product of progesterone. Pregnanediol is excreted in the urine and the quantity present is an indication of the activity of the corpus luteum.



The chief function of progesterone is to cause a type of growth of the endometrium which prepares it for implantation of the fertilized ovum. If conception does not occur, the corpus luteum atrophies and ceases to supply progesterone and this results in a breakdown of the progestational endometrium of the uterus with subsequent hemorrhage of non clotting blood, i.e., menstruation. If conception does take place, the corpus luteum persists because of the influence of prolactin (a pituitary hormone), and progesterone maintains the endometrium.

### SELF-TESTING QUESTIONS

- 21 What is an androgen? Name two androgens.
- 22 At what time during the menstrual cycle is conception most likely to occur? Why?
- 23 What is the endometrium?
- 24 What is a graafian follicle?
- 25 What is the corpus luteum?
- 26 What effects do estrogens have in the female?
- 27 What is the action of progesterone?
- 28 Name three estrogens.

## VI. THE PITUITARY GLAND AND ITS HORMONES

The pituitary gland (hypophysis) is a small structure situated at the base of the brain and has frequently been referred to as the "master endocrine organ" because it controls or influences several of the other endocrine structures as well as regulates many other body processes. Anatomically, the pituitary is divided into three portions (1) the anterior pituitary, (2) the posterior pituitary, and (3) the pars intermedia or the intermediate portion. Much more has been learned of the function of the anterior pituitary than of the other two portions. Knowledge of the hormonal function of the pituitary has been acquired as a result of the following

types of animal experimentation: (1) noting the physiological effects of removal of the gland; (2) observing the ameliorative effects resulting from injection of extracts of the pituitary into animals with this gland removed; (3) witnessing the results produced in normal animals by the injections of extracts of the gland.

Removal of the whole pituitary or merely the anterior portion produces the following effects:

1. Cessation of growth.
2. Atrophy and loss of function of the gonads (ovaries and testes).
3. Atrophy of the thyroid gland.
4. Cessation of lactation in a lactating animal.
5. Atrophy of the adrenal cortex.
6. Improvement in the condition of a diabetic animal.

All of these phenomena can be reversed by the injection of extracts of the anterior pituitary glands obtained from other animals. More exacting studies and the chemical separation and purification of the crude extracts have indicated that there are several

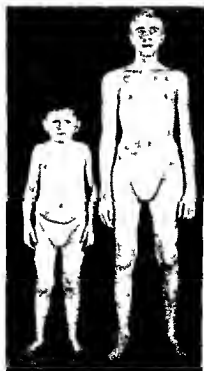


Fig 6—Hypopituitarism Comparison of dwarf of 17 years with a normal youth of the same age. What are the main functions of the pituitary? Courtesy, Dr R A Shipley

rather than one single hormone secreted by the anterior pituitary. Six of these hormones have been obtained as relatively pure chemical compounds during the past ten years and all of these are of a protein nature. In that proteins are such complex compounds, none of the pituitary hormones has been synthesized in the laboratory. As a result, all of the pituitary hormones that are used therapeutically must be obtained from natural sources. For this reason, such preparations are very expensive.



Fig. 7—Acromegaly. The disease is characterized by progressive enlargement of the bones in the face, hands, and feet, and large tongue. Overactivity of the anterior lobe of the pituitary gland in childhood produces what condition? Courtesy, Dr. R. A. Shipley.

### The Growth Hormone:

The cessation of growth in animals with their pituitary removed<sup>7</sup> as well as the increase in growth of normal animals when given pituitary extracts, has provided evidence for a growth hormone. There is also clinical evidence for a growth hormone based on the observation of patients with pituitary disorders. For instance, if the pituitary is hypofunctional during growth, a "pituitary dwarf" will result (Fig. 6). Excessive production of growth hormone also is observed in patients who have a certain type of tumor of the anterior pituitary. If excessive secretion of the hormone occurs



during childhood, proportional body growth is stimulated and a "pituitary giant" results. The giants observed in circus sideshows are usually examples of this type of pituitary disorder. However, if the stimulation occurs after closure of the epiphyses of certain long bones, a disproportionate growth pattern is observed and such individuals grow in a grotesque manner. This condition is referred to as acromegaly (Fig. 7).

### **Gonadotropic Hormones of the Anterior Pituitary:**

The pituitary is responsible for the development and maintenance of function of the gonads. Hypofunction of the gland results in decreased gonadal activity; and removal of the pituitary causes a loss of sexual function. Administration of pituitary extracts to immature animals produces precocious sexual maturity. Careful study of this gonadotropic activity has indicated that there are two gonadotropic hormones and these have been chemically separated and prepared as relatively pure compounds. Their action is quite different in the male and in the female. Several names have been applied to these two hormones and this has made their cognizance quite complex; but an understanding of their function is quite important.

**THE FOLLICLE-STIMULATING HORMONE (FSH, GAMETOGENIC HORMONE, PROLAN A):** In the female, this hormone stimulates the growth of graafian follicles in the ovary. As was discussed in the section on female hormones, the growth and maturation of a follicle are an important phase of the female sexual cycle. In the absence of the hormone, follicles do not develop and as a result, the estrogens which they produce are not available for action on the endometrium of the uterus. In the male, FSH stimulates the sperm-forming tissues of the testes which might be considered analogous to the ovum-producing follicles of the ovary.

**THE LUTEINIZING HORMONE (LH, INTERSTITIAL CELL-STIMULATING HORMONE, PROLAN B):** In the female, this hormone causes luteinization of the ruptured graafian follicle and this results in a corpus luteum. It has already been pointed out that the corpus luteum also produces an important hormone. In the male, luteinizing hormone stimulates the interstitial cells of the testes which are responsible for the production of the male sex hormone testosterone.

The relationship of the pituitary gonadotropic hormones and the female sex hormones to the menstrual cycle can be visualized

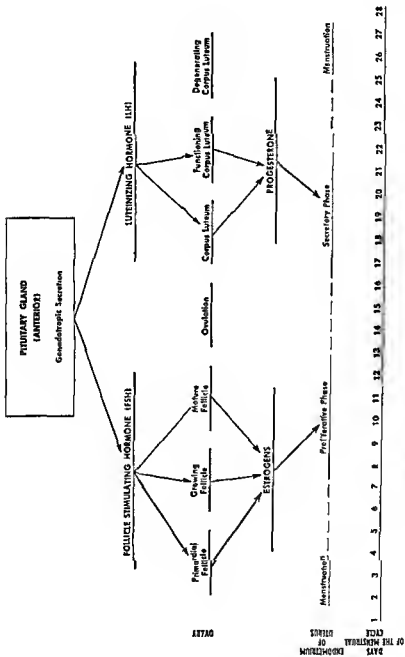


Fig 8—Endocrine Relationships of the Menstrual Cycle. Courtesy, Helen Murray.

in Figure 8. During the *first phase of the cycle*, there is a predominant secretion of follicle-stimulating hormone by the anterior pituitary. This causes the development and maturation of a graafian follicle. The maturing follicle in turn secretes estrogens which cause the endometrium of the uterus to develop and also produce estrus in animals. With ovulation, which occurs approximately at the 14th day of the cycle, the pituitary secretes a predominant quantity of luteinizing hormone that stimulates the development of the corpus luteum. The corpus luteum produces the hormone progesterone which maintains the endometrium in a condition favorable for reception of the fertilized ovum. Towards the end of the cycle, the output of luteinizing hormone by the pituitary diminishes and the corpus luteum in turn atrophies and ceases to supply progesterone. In the absence of progesterone, the uterine wall is no longer maintained and with its degradation, menstruation occurs. In case of conception, the corpus luteum is maintained by the stimulating effect of prolactin, another anterior pituitary hormone which will be discussed later.

A substance similar to pituitary gonadotropins and called chorionic gonadotropin is produced by the placenta and appears in the urine in relatively large quantities soon after the beginning of pregnancy. The presence of large amounts of this chorionic gonadotropin is the basis for the Aschheim-Zondek and the Friedman tests for pregnancy. The injection of pregnancy urine containing this gonadotropin into immature female mice (A-Z test) or into unmated female rabbits (Friedman test) results in the rapid development and rupture of a graafian follicle within a period of 1 to 4 days. The results of such tests can be determined by macroscopic observation of the ovary. The male frog is also being employed as a test animal for the demonstration of chorionic gonadotropin in urine (i.e., for a pregnancy test). Injection of urine containing chorionic gonadotropin into the dorsal lymph sac of the male frog causes the appearance of spermatozoa in the frog's urine within one or two hours. Sperm can readily be seen by examining the frog's urine on a slide under a microscope.

### **The Lactogenic Hormone of the Anterior Pituitary (Prolactin):**

The process of lactation subsequent to parturition is under the control of a hormone of the anterior pituitary which is called prolactin. This hormone was the first of the pituitary hormones obtained as a pure chemical compound and has been found to be a

protein with a molecular weight of approximately 25 000. The hormone alone is not capable of causing lactation but functions in the breast that has been hypertrophied by estrogens. The combined administration of estrogens and prolactin will produce lactation even in the male species. There appears to be some inhibitor to prolactin that is present during the course of pregnancy but following delivery the restraining factor is removed and the secretion of milk occurs. This inhibitor substance is believed to originate in the placenta. Prolactin also is responsible for the maintenance of the corpus luteum during pregnancy.

### **The Thyrotropic Hormone (Thyrotrophin)**

The activity of the thyroid gland is under the regulation of a thyrotropic hormone which is secreted by the anterior pituitary. Removal of the pituitary results in a decreased thyroid function and injection of the hormone stimulates the thyroid and may produce evidences of hyperthyroidism. This hormone has been isolated and identified as a protein. It appears likely that certain thyroid dysfunctions seen in clinical practice can be attributed to an abnormality of thyrotrophin secretion by the anterior pituitary.

### **The Adrenocorticotrophic Hormone (ACTH)**

The adrenal cortex is under the control of a hormone secreted by the anterior pituitary. This hormone is called the adrenocorticotrophic hormone or ACTH. In the absence of the stimulating effect of ACTH the adrenal cortex will atrophy and evidences of adrenal cortical insufficiency will appear. Much has been learned in recent years of the effect of ACTH and the adrenal cortex in overcoming stresses such as poisoning by chemicals or bacterial toxins, bleeding, crushing injuries, burns and exposure to severe cold. When such a stress develops the pituitary is stimulated and it releases increased quantities of ACTH. The ACTH in the circulating blood in turn causes release of cortisone and other adrenal cortical hormones. These provide the protection against the stress.

ACTH is a low molecular weight protein which is prepared from animal pituitaries in much the same way that insulin is prepared from animal pancreases. ACTH is non antigenic and is widely used in medical practice. The biologically active portion of the ACTH molecule has recently been synthesized (p 401). Its uses are quite comparable to those of cortisone which was discussed in an earlier section.

### **The Diabetogenic Hormone of the Anterior Pituitary**

In the discussion of insulin, it was mentioned that the administration of extracts of the anterior pituitary would produce disturbances of carbohydrate metabolism similar to those noted in diabetes. It has also been observed that an animal having diabetes as a result of the removal of the pancreas will be beneficially affected by removal of the anterior pituitary gland. This has led to the belief that the anterior pituitary may secrete a hormone which antagonizes insulin. In other words, this hormone tends to produce diabetes whereas insulin tends to prevent diabetes. Accordingly, this hormone has been called the diabetogenic hormone. At the present time, this hormone has not been purified and the exact mechanism of its action is not clearly defined. It is quite possible that the effect is due to the action of the growth hormone and the adrenocorticotrophic hormone. However, it seems that normal carbohydrate metabolism is brought about by a proper ratio of insulin and diabetogenic hormone. If there is an excess of diabetogenic hormone or a deficiency of insulin, a diabetic state will result, whereas, if the pendulum swings the other way and there is either an excess of insulin or a deficiency of diabetogenic hormone, a state of hypoglycemia will result with ultimate "insulin shock."

Since the anterior pituitary is responsible for the elaboration of many hormones, it can be readily understood that disorders of the pituitary might result in complex disease states due to an imbalance of the various hormones. One such example of this is Cushing's syndrome (Fig 9) which is caused by an adenoma (tumor) of a certain type of cell in the gland. In this condition there is formed an excess of the adrenocorticotrophic hormone and the gonadotropic hormones.

### **The Posterior Pituitary:**

The posterior portion of the pituitary is smaller than the anterior part and because of its anatomical position, it is virtually impossible to remove it without injury to the anterior pituitary. This has made the study of the normal function of the posterior pituitary extremely difficult. There is some evidence that damage to this portion of the gland results in polyuria (increased urine output). This suggests that the posterior pituitary secretes a hormone that regulates urinary volume. There is a clinical condition known as diabetes insipidus which is characterized by an excessive thirst and the excretion of very large urine volumes.



Fig. 9—Cushing's Disease. Notice obesity of the face and neck as the result of a pituitary tumor. Tumors of what other glands may cause this disease? Courtesy, University Hospitals, Cleveland, Ohio.

Additional evidence for the secretion of an antidiuretic hormone is furnished by the fact that extracts of the posterior pituitary will reduce urine volumes to normal when administered to such patients.

Chemical fractionation of posterior pituitary extracts has resulted in the separation of two fractions which have been called vasopressin (Pitressin) and oxytocin (Pitocin). Whether these substances are true hormones or merely compounds with specific pharmacological actions is a matter of debate at the present time. Vasopressin will increase blood pressure and has been used to combat the low blood pressure of shock following severe injury or extensive surgical procedures. It also possesses the principle which decreases urinary output in diabetes insipidus. Oxytocin has a powerful stimulating action on the contraction of the smooth muscles of the uterus. This property is made use of in certain cases encountered in obstetrical practice.

No known endocrine function is ascribed to the intermediate portion of pituitary (pars intermedia) in mammals.

#### SELF-TESTING QUESTIONS

- 29 What methods have been successfully employed to demonstrate the endocrine activity of the pituitary?
30. Name five effects that may be produced by removal of the anterior pituitary.

- 31 Name three clinical conditions that are due to excess or deficiency of growth hormone
- 32 Briefly discuss the role of follicle stimulating hormone (FSH) luteinizing hormone (LH) estrogens and progesterone in the menstrual cycle
- 33 What are vasopressin and oxytocin? Indicate one use each might have in medical practice
- 34 What is the chemical nature of the anterior pituitary hormones?
- 35 What is the basis for the male frog pregnancy test?

## VII THE GASTROINTESTINAL HORMONES

The fact that hormones play an important role in digestion has already been pointed out in a previous chapter. However, these relationships will be briefly reviewed. When there is no food in the alimentary canal the digestive apparatus is relatively quiescent but following the ingestion of a meal the whole system actively functions in a beautifully synchronized manner. This is due to both nervous and humoral (hormonal) control.

### Gastrin

When food enters the stomach a hormone is released from the pyloric region which is absorbed into the blood. This hormone is called gastrin. Its presence stimulates both muscular contractions and secretory activity on the part of the stomach. Thus it produces a flow of gastric juice containing increased quantities of hydrochloric acid and pepsin. The chemical nature of the hormone gastrin is a matter of some dispute. There is some evidence that the hormone is a simple chemical substance identical with the amino acid derivative histamine. It is known that histamine has a powerful stimulating effect on gastric activity. However there is also some evidence to suggest that gastrin is a protein like hormone.

### Secretin

This is one of the hormones which is released when food enters the duodenum. It stimulates the production and flow of pancreatic juice. It is of considerable historical interest that secretin was the first recognized hormone. It was discovered in 1902. Secretin has been isolated as a pure chemical compound and has been identified as a polypeptide.

### Cholecystokinin

This is a third gastrointestinal hormone. It is liberated into the blood stream when food enters the duodenum. When blood containing the hormone passes through the walls of the gallbladder it causes the muscles to contract and concentrated gallbladder

bile is forced through the ducts into the duodenum. Thus far the hormone has not been obtained in a purified state

### Enterogastrone:

In the process of digestion, one of the functions of the stomach is to act as a reservoir which stores the ingested food until it can be digested and absorbed. This is necessary since the intestine can handle only small quantities of food at a time. It has been found that the emptying of the stomach is controlled by a hormone (enterogastrone) which originates in the lining of the small intestine. When food enters the small intestine, this hormone is released into the blood and on reaching the stomach it temporarily inhibits further gastric secretory activity by emptying of gastric contents into the duodenum. Enterogastrone has not been prepared as a pure compound. A somewhat related substance called urogastrone with a similar physiological effect can be obtained from urine. This material has been used to treat peptic ulcer.

### Enterocrinin (Enterin):

This hormone also originates in the mucosa of the small intestine and is released when food enters the duodenum. Its physiological effect is to stimulate secretion of intestinal juice (*succus entericus*). At the present time, enterocrinin has been obtained only in crude extracts

### SELF-TESTING QUESTIONS

- 36 What was the first hormone discovered? When did this occur?
- 37 What is the action of enterogastrone?
- 38 What hormone stimulates the evacuation of the gallbladder?
- 39 Where does secretin originate? What is its action?
- 40 What is gastrin?

### SUGGESTED ACTIVITIES

#### I THOUGHT PROVOKING QUESTIONS

- 1 Why must insulin be injected rather than given orally?
- 2 What effect would the administration of thyrotropic hormone have on the basal metabolism of a normal individual?
- 3 What laboratory chemical examinations are useful in the diagnosis of parathyroid disorders?
- 4 Describe the treatment of a patient with Addison's disease
- 5 Suggest how hormones might be employed to produce menstruation in a castrated female
- 6 How would you distinguish between a cretin dwarf and a pituitary dwarf?



- 7 Make a list of all the substances which are known to contain the steroid nucleus
- 8 Discuss the digestive processes indicating the relative role of hormones and enzymes
- 9 Make a list of all the diseases in which the principal disturbance is an excessive or deficient secretion of hormones
- 10 Name three hormones that have been prepared synthetically and which are useful clinically
- 11 Name the clinically useful hormone made from animal tissues

## II VOCABULARY TESTING OF NEW TERMS

endocrine	desoxycorticosterone	thyroxine
hormone	estrogen	progesterone
ductless gland	estradiol	metakentrin
insulin	androgen	oxytocin
hypoglycemia	testosterone	vasopressin
hyperthyroidism	acromegaly	endometrium
adrenal medulla	myxedema	ovulation
epinephrine	cretinism	gastrin
hypoparathyroidism	thylakentrin	enterogastrone
Addison's disease	thyroglobulin	secretin
ACTH	thyrotropic hormone	anterior pituitary
graafian follicle	cholecystokinin	prolactin
cortisone	chorionic gonadotropin	enterin

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Prepare a report based on outside reading on one of the following subjects (a) Plant hormones (b) Antihormones (c) Commercial production of insulin (d) Commercial production of thyroxine (e) The use of estrogens in the treatment of prostatic carcinoma (f) Stress reactions in disease
- 2 Present a clinical history and description of a patient on your ward suffering from some endocrine disturbance
- 3 Consult the book published by the American Medical Association 1954 *Glandular Physiology and Therapy* and prepare a report based on one of the topics discussed in this text as suggested by your instructor

## LABORATORY CHEMISTRY

Time and facilities make it impractical to carry out any laboratory experiments on the hormones

## VITAMINS AND MILK

## CHAPTER OUTLINE

- |                                      |                                      |
|--------------------------------------|--------------------------------------|
| I. <b>INTRODUCTORY DISCUSSION</b>    | V. <b>VITAMIN D</b>                  |
| (a) Vitamins and hormones            | (a) Functions and deficiency effects |
| (b) Vitamin complexes                | (b) Sources                          |
| (c) Vitamin assay                    | (c) Assay and unitage                |
| (d) Vitamin unitage                  | (d) Requirements                     |
| II. <b>VITAMIN A</b>                 | VI. <b>VITAMIN E</b>                 |
| (a) Deficiency effects               |                                      |
| (b) Properties                       | VII. <b>VITAMIN K</b>                |
| (c) Sources                          |                                      |
| (d) Assay and unitage                | VIII. <b>VITAMINS IN NUTRITION</b>   |
| (e) Requirements                     | IX. <b>MILK</b>                      |
| III. <b>VITAMIN B COMPLEX</b>        | (a) As a food                        |
| (a) Thiamine ( $B_1$ )               | (b) Composition                      |
| (b) Riboflavin ( $B_2$ )             | (c) Modified milk                    |
| (c) Niacin (nicotinamide)            | (d) Pasteurization                   |
| (d) Pyridoxine ( $B_6$ )             | (e) Lactic acid milk                 |
| (e) Pantothenic acid                 | (f) Fuel value                       |
| (f) $B_{12}$                         | (g) Protein content                  |
| IV. <b>VITAMIN C</b>                 | (h) Mineral content                  |
| (a) Functions and deficiency effects | (i) Vitamin content                  |
| (b) Sources                          |                                      |
| (c) Assay and unitage                |                                      |
| (d) Requirements                     |                                      |

## I. INTRODUCTORY DISCUSSION

During the early years of the present century it was found that a diet consisting of pure carbohydrates, fats, and proteins, together with the necessary minerals and water, was not an adequate one. Animals fed on such a purified diet did not show proper growth, and failed in health. The addition of small quantities of natural foods, such as hutter and milk, usually corrected such conditions and health and growth became normal. These natural foods were thought, therefore, to contain certain factors essential to correct nutrition.

Some of the first experiments in this phase of nutrition were conducted by Funk, a Polish chemist. Funk succeeded in extracting from rice polishings a substance which was highly effective in combating a disease known as beriberi, which is contracted through faulty diet. His analysis indicated that this substance was an amine, and inasmuch as it appeared to be essential to life he coined the name "vitamine." This word has since been changed to

"vitamin," and it is now applied to a series of substances which are essential to proper nutrition without regard to the chemical structures of the substances

The study of vitamins has become an extremely important development in the field of foods and nutrition. It is now known that a number of diseases which were prevalent in the past were due to a lack of certain vitamins or "food accessories." Scurvy, beriberi, and rickets are typical examples of the deficiency diseases, and as such they can be corrected by proper dietary treatment.

### Vitamins and Hormones

In a number of respects the vitamins are similar to the body hormones. Thus, like the hormones they exhibit specific activities, are effective in small amounts, and in general are essential for the proper growth and health of the body. In fact, the term "food hormones" was at one time proposed for vitamins. However, it must be kept in mind that the vitamins are supplied normally in foods, whereas the hormones are synthesized in the body itself. Certain B vitamins, and vitamin K, are synthesized to a limited extent in the intestines by bacterial activity on food residues. Studies have proven that vitamins, hormones, and body enzymes operate in close association to control metabolism.

### Vitamin Complexes

The number of vitamins has grown rapidly in recent years until at the present time some twenty to twenty-five accessory food factors are recognized. Undoubtedly more will be discovered. In some cases what at first was considered to be a single vitamin has proven under further investigation to be a complex consisting of a number of individuals, each possessing specific activities. For illustration, the original vitamin B is now known to be a complex of some eight or ten different factors. The correct terminology, therefore, is vitamins B, or the vitamin B complex. Members of a complex are often best known by their chemical names, for example, thiamine hydrochloride and riboflavin are two members of the B complex.

One of the earliest classifications of vitamins was made on the basis of solubility in water and in fats. This classification continues to have merit, and vitamins are characterized as water soluble or fat soluble.

### Vitamin Assay:

The rat has been widely used to determine the vitamin content of foods and the potency of vitamin preparations, and to study the symptoms arising from dietary deficiencies. Rats in most instances react as do humans to variations and deficiencies in the diet. One noteworthy exception occurs in the case of vitamin C; rats require little or none, and for this reason they are not suitable animals for investigating this factor. In this connection the guinea pig has proven valuable as a substitute for the rat.

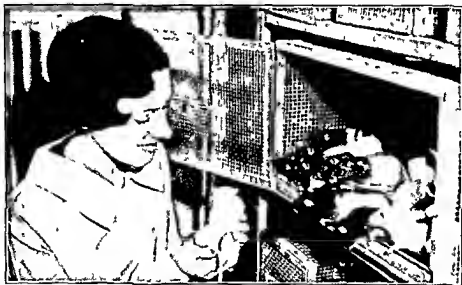


Fig 1—Rats Used in Diet Deficiency Tests. Rats are used in biological assays to determine vitamin strength. Why are rats used in preference to most other animals? Courtesy, National Oil Products Co

When animals are used in the study of a specific dietary deficiency a control group is given a diet which is adequate in all respects, while a similar experimental group is provided with a diet adequate in all respects except one—it is lacking in the single factor or vitamin to be studied. All animals are weighed at regular periods, and conditions such as health, appearance of skin and hair, activity, appetite, sex response, etc. are carefully noted. In time those on the experimental diet lose weight and develop characteristic symptoms which can be attributed to the absence of the vitamin (avitaminosis).

The use of experimental animals for the determination of vitamin content and the study of deficiency symptoms usually gives excellent results. Unfortunately such biological methods are time consuming, several weeks must elapse before conclusive data are available. Gradually, as the chemical structures and reactions of the vitamins are revealed, chemical methods of testing for potency become feasible. The vitamin C content of a food, for example can now be determined rapidly and with considerable accuracy by methods of quantitative analysis. This is possible because vitamin C is a pure chemical substance known as *l* ascorbic acid, and as such it exhibits a characteristic chemical behavior. It must be emphasized that the biological methods of assay which employ experimental animals are today very important and widely used. The newer analytical methods of chemistry are not displacing but rather supplementing, the older approach.

### Vitamin Unitage

Various methods are in use for expressing the vitamin content of foods and diets in specific units of measurement. The procedures used for determining vitamin potency have been varied for this and other reasons considerable confusion has arisen in vitamin unitage. As the chemical structures of the vitamins become known it is desirable to express the quantities and requirements in terms of weight of pure substance. Several examples may be helpful here. At one time the unit of vitamin C was defined as 'that amount which, when fed as a daily allowance, just suffices to afford full protection from scurvy in a standard guinea pig'. A more accurate unit is the International unit (IU), this is defined as 0.05 milligram (mg) of pure crystalline *l* ascorbic acid (vitamin C). The IU is identical with the United States Pharmacopoeia unit (USP unit). In some more recent tabulations of vitamin requirements the recommended daily allowance, when possible, is stated in milligrams or micrograms of pure substance (1 milligram is equal to 1000 micrograms).

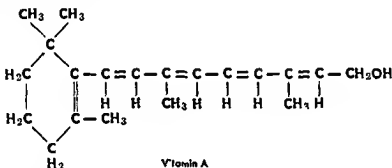
### SELF-TESTING QUESTIONS

- 1 From the foregoing discussion formulate a definition for vitamins
- 2 Why were vitamins originally called *vitamines*? Why was the name changed?
- 3 In what respects are vitamins and body hormones similar? Wherein do they differ?

- 4 What is the meaning of a vitamin complex?
- 5 From the standpoint of solubility, what are the two main classes of vitamins?
- 6 Outline the steps in the biological method of vitamin assay
- 7 What are the various systems in use for designating amounts of vitamins?

## II VITAMIN A

Vitamin A is a fat soluble factor, and is known also as the anti-xerophthalmia vitamin. This substance has been isolated in pure form and the chemical structure has been established. Vitamin A is a complex, high molecular weight, primary alcohol which contains a six carbon atom ring.



Not only vitamin A, but a number of substances called its precursors are found in nature. The precursors may be termed provitamins. In the animal body they are broken down to provide the active vitamin. The four recognized precursors of vitamin A are the  $\alpha$ ,  $\beta$ , and  $\gamma$  carotenes, and a carotenoid called cryptoxanthin.  $\beta$  Carotene is the most abundant of the provitamin A group; it is available commercially in an oil solution which can be employed to correct vitamin A deficiency. There is some evidence that there are two varieties of this vitamin and the designations  $A_1$  and  $A_2$  may become necessary.

### Deficiency Effects

As pointed out by the term "anti xerophthalmia factor," a lack or deficiency of this vitamin in the diet over a period of time results in an eye disease. Xerophthalmia is apparent as dryness and scal-

ness of the skin and an increased susceptibility to eye infections. One of the symptoms first noticed is nyctalopia or "night blindness"; this results when there is a lag in the regeneration of the visual purple which is essential for clear, sharp vision. As a matter of fact, the degree of night blindness, or impairment of adaptation to darkness, can be used clinically as a measure of vitamin A deficiency.

Severe vitamin A deficiency leads to disturbances other than ocular. The respiratory, alimentary, and genitourinary tracts may be affected through the replacement of normal epithelial tissue with pathological tissue. In general, body resistance to various types of infection is lowered. This function of vitamin A has led to the use of the term "anti-infective" vitamin. However, vitamin A must not be considered as a specific remedy for colds, respiratory afflictions, and related disorders; in itself it cannot destroy disease bacteria. The vitamin is anti-infective in the sense that it aids in maintaining healthy epithelial cells and tissue; this is the body's first line of defense in resisting infection.



Fig 2—Vitamin A deficiency. Note "goose flesh" appearance of skin of thighs due to follicular hyperkeratosis.

**Properties:**

Vitamin A is insoluble in water, but soluble in fats and oils. Experiments have proven that it is fairly stable to heat, and to acids and bases. It is, however, destroyed by free oxygen and other oxidizing agents. Ordinary cooking procedures do not destroy vitamin A to any appreciable degree.

**Sources:**

Vitamin A and its precursors are abundantly supplied by nature. In plants there is a correlation between greenness and yellowness of color and the vitamin A or carotene content. Green leaf lettuce,

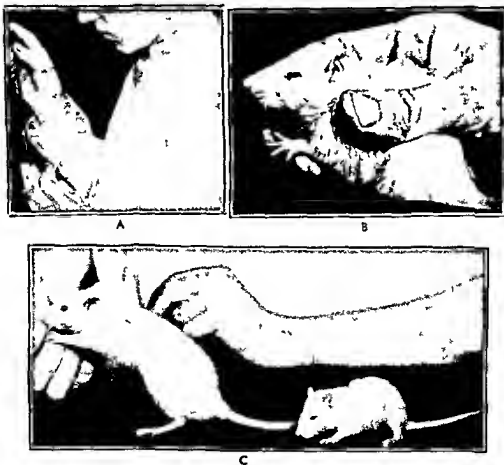


Fig 3—Vitamin A Deficiency (A) A rat receiving his daily treatment (B) Typical eye infection due to lack of vitamin A. (C) Two rats with differences in growth due to vitamin deficiencies.



cabbage, peas, and green beans are rich sources. Carrots and sweet potatoes are also excellent sources; during World War II carrot juice was prescribed for aviators to combat night blindness.

Certain foods from animal sources supply vitamin A in good amount. The fish liver oils such as cod and halibut have long been used to supply vitamin A. Butter, whole milk, and eggs are important sources. Vitamin A can be stored in the body, largely in the liver, for a considerable time.

### Assay and Unitage:

Vitamin A gives an intense blue color with antimony chloride; consequently it becomes possible to determine vitamin A content colorimetrically with this reagent. Spectrophotometric methods of assay, based upon absorption of ultraviolet light, are coming into prominence. Biological methods which employ rats are widely used despite the fact that weeks are required for collecting data.

The international unit (I.U.) of vitamin A, identical with the U.S.P. unit, is defined as the growth promoting activity for rats of 0.6 microgram (0.0006 milligram) of standard  $\beta$ -carotena.

### Requirements:

The recommended minimum daily allowance of vitamin A is generally given as 5000 I.U. for adults and children alike, with a somewhat greater quantity, about 8000 I.U., recommended for nursing and pregnant women. One to two teaspoonfuls of codliver oil will supply this amount.



Fig 4—A Deficiency Causes Infection. Illustrating a case of xerophthalmia due to lack of vitamin A. A deficiency of vitamin A may produce what other infections? Courtesy, John Anderson Thurman

## SELF-TESTING QUESTIONS

- 8 What is a provitamin? Illustrate What other name applies to such a substance?
- 9 In what sense is vitamin A anti infective?
- 10 What is night blindness? Give the medical term for this
- 11 Give at least three different ways of testing for vitamin A
- 12 What pure chemical substance is used as a reference in vitamin A unitage? State the relationship of this substance to vitamin A

## III. VITAMIN B COMPLEX

Early in nutritional studies it was found that a substance present in rice polishings was effective in overcoming polyneuritis in pigeons and beriberi in man In the past beriberi has been a major disease in the Orient Takaki, a Japanese naval medical officer, demonstrated that beriberi could be cured and prevented by correcting the diet The active factor which accomplishes this was given the name vitamin B Further investigation has shown that what was at first supposed to be one factor is in reality a complex All members of this complex are water soluble Some are essential in human nutrition, others prevent nutritional diseases in animals The best known and likely most important members of the complex are noted here, and will be considered in order

Thiamine (vitamin B<sub>1</sub>, thiamine hydrochloride, aneurin)

Riboflavin (vitamin B<sub>2</sub>, vitamin G)

Niacin (nicotinic acid, nicotinamide, P P factor)

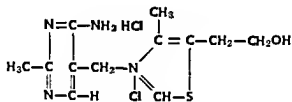
Pyridoxine (vitamin B<sub>6</sub>)

Pantothenic acid (filtrate factor)

B<sub>12</sub>

Thiamine (B<sub>1</sub>)

*This important member of the vitamin B complex is known as the anti neuritic vitamin, anti beriberi vitamin, aneurin, and appetite stimulating vitamin, and by the chemical name thiamine, or thiamine hydrochloride The substance was first extracted in pure form from rice polishings, and shortly thereafter, in 1937, its chemical synthesis was announced The structural formula for the hydrochloride is presented below It is important to note that thiamine contains the elements N, S, and Cl, in addition to C, H, and O, and that like vitamin A it is a complex, high molecular weight, primary alcohol*

Thiamine Hydrochloride (B<sub>1</sub>)

**FUNCTIONS AND DEFICIENCY EFFECTS:** Certain names for thiamine noted above suggest the nature of the pathological conditions which result when there is a deficiency of the vitamin in the diet. The disease of polyneuritis, known as beriberi in man, is specifically associated with a lack of thiamine. Polyneuritis can be produced in animals by withholding thiamine from the food. A deficiency of B<sub>1</sub> is at first evidenced by a loss of appetite, weakness, fatigue, loss of weight, and impaired digestive processes. In more serious cases the advanced symptoms are polyneuritis (beriberi in man) and cardiovascular disturbances. It has been shown that thiamine is essential for the proper functioning of the nervous system and the gastrointestinal tract. There is generally accepted evidence that thiamine is required for the proper metabolism of carbohydrates. In the absence of the vitamin the pyruvic acid which is produced in the breakdown of carbohydrates is not oxidized, but accumulates in the body and produces neuritic conditions.



While there are but few instances of beriberi in this country there is nevertheless little doubt but what a considerable proportion of the population suffers at one time or another from marginal thiamine deficiency. Vitamin B<sub>1</sub> cannot be stored in the body for any appreciable length of time, but must be furnished rather continuously in properly selected foods or supplementary preparations. The highly refined foods of today are

Fig 5—Vitamin B Complex Deficiency (Thiamine) Beriberi Legs



Fig 6—Vitamin B<sub>1</sub> (Thiamine Chloride) Prolonged deficiency of this vitamin checks growth in young animals causes loss of appetite and results in degenerative changes in the nervous system (left) Administration of two to three International units (0.006 to 0.009 mg) of thiamine chloride will cure the symptoms (right)

usually deficient in thiamine

**PROPERTIES** Thiamine is a water soluble factor. It is quite stable up to a temperature of 100° C in acid medium, but experimentation has shown that it is destroyed by heat in neutral or alkaline solution.

**SOURCES** The best natural sources of thiamine are the whole cereal grains, liver, lean meat, nuts, yeast, and a number of the green vegetables.

Modern processes in milling grains for the production of refined flour may remove up to 90 per cent of the original thiamine content of the whole grain. As a result of decortication of grain, prolonged cooking processes, and the wasting of cooking liquors, the thiamine content of raw foods may be removed or destroyed to such a degree that the diet is deficient in this factor.



Fig 7—Girl with Beriberi as a Result of Vitamin B Deficiency. Why should vitamin B be included in our diet? Courtesy CLINICAL PEDIATRICS Appleton Century Co

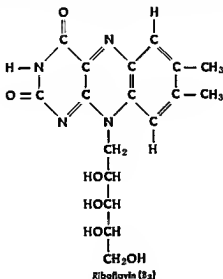
**ASSAY AND UNITAGE** A variety of methods have been developed for the detection and assay of thiamine. The biological rat curative method is reliable, but time consuming. The oxidation of thiamine with potassium ferricyanide produces a fluorescent compound named thiochrome, and the intensity of the fluorescence is a measure of the thiamine content. Thiamine has been found to hasten certain alcoholic fermentations promoted by yeast, and this affords a method of assay. In addition there are a number of colorimetric procedures.

The USP unit of vitamin B<sub>1</sub>, which is identical with the IU, is defined as the vitamin B<sub>1</sub> activity of 3.0 micrograms (0.003 milligram) of standard thiamine hydrochloride.

**REQUIREMENTS** The recommended daily allowance of thiamine ranges from 700 to 900 IU, depending upon sex, age, etc. This amounts to from 1.0 to 2.0 milligrams.

### Riboflavin (B<sub>2</sub>)

Riboflavin, vitamin B<sub>2</sub>, is one of the heat stable factors of the vitamin B complex. In the past it has been known as vitamin G. Riboflavin has been isolated from natural sources, and its chemical structure has been proven through synthesis. There are several important groups in the riboflavin molecule, among them one derived from a sugar called ribose. The structure of riboflavin is given below.



**DEFICIENCY EFFECTS:** Symptoms of insufficient riboflavin are lesions at the corners of the mouth accompanied by a characteristic reddening of the lips; the latter condition is termed cheilosis. Usually these conditions are promptly relieved by riboflavin therapy. Lesions about the eyes, keratitis, and a skin condition termed "sharkskin" can often be traced to a riboflavin deficiency.

**SOURCES:** Riboflavin is of fairly wide occurrence in natural foods; in general, sources rich in thiamine also supply riboflavin. Lean meats, green top vegetables such as beet tops and kale, and whole grains are excellent sources. Riboflavin is stable towards heat, especially so in acid medium. Its stability is greatly decreased by alkali. Like thiamine it cannot be stored in the body for any length of time.

**ASSAY AND UNITAGE:** Rat curative methods continue important in riboflavin assay. Riboflavin fluoresces under ultraviolet light,



Fig. 8—Riboflavin. This part of vitamin B complex is essential to the consumption of oxygen by body cells, promotes growth, and is necessary for skin health. Rat with dermatitis (left) cured by riboflavin (right).

and the intensity of such fluorescence becomes a measure of the riboflavin concentration. Recently a microbiological method has been developed which depends upon the fact that certain lactic acid bacteria require this vitamin in their production of lactic acid.

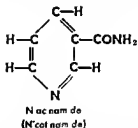
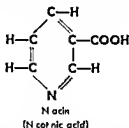
No International or U.S.P. unit exists for riboflavin. Inasmuch as the pure substance is available, requirements, etc., can be stated in terms of milligrams.

**REQUIREMENTS:** It is known that riboflavin is essential to man, and to dogs, cats, rats, and chicks. The suggested daily allowance for humans is from 1.0 to 2.5 milligrams.

### Niacin (Nicotinamide):

Niacin is the most recent name for a member of the vitamin B complex which is known also as nicotinic acid, nicotinamide, and Goldberger's P-P factor (pellagra-preventive). Long before niacin

was found to function as a vitamin its structure and methods of preparation were known to chemists



**FUNCTIONS AND DEFICIENCY EFFECTS** Niacin is a specific cure for blacktongue in dogs and its analog, pellagra, in man. Pellagra is a disease which prevails especially among the poorer people of southern United States who subsist on a diet which may be largely corn meal, fat pork, and molasses. This disease is also known in central and southern Europe. Pellagra is characterized by skin lesions, diarrhea, and mental disorders, or as Harris states, by the three d's—dermatitis, diarrhea, and dementia. People afflicted with pellagra are invariably cured when fresh meat, vegetables, etc., are added to the diet. Niacin has been found as a constituent of certain coenzymes which function in cellular respiration.

**SOURCES** The best sources of niacin are the fresh organ meats such as liver, heart, and kidney, and also yeast, fish, whole wheat,

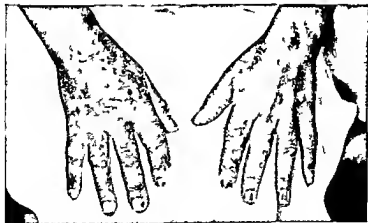


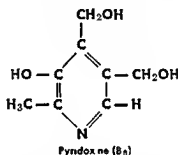
Fig 9—Nicotinic Acid Is a Cure for Pellagra. Left hand of pellagra victim showing the frightful skin condition which is one of the symptoms of the disease. Right hand of same victim after treatment with nicotinic acid.

milk and eggs. It is one of the most stable of the vitamins and is very little affected by heat, acid, and alkali. Very little, therefore, is lost in ordinary cooking methods except when cooking liquors are discarded.

**REQUIREMENTS** There is difficulty in determining with any degree of accuracy the amount of niacin needed in human nutrition. The recommended daily allowance is from 4.0 to 20.0 milligrams, depending upon age, sex, activity, pregnancy, etc.

### Pyridoxine (B<sub>6</sub>)

Pyridoxine, vitamin B<sub>6</sub>, bears a structural relationship to niacin, inasmuch as both are derivatives of pyridine.



A deficiency of this factor in the diet of rats causes a dermatitis which is accompanied by considerable swelling and edema, especially of the paws, ears, nose, and lips. The condition is described as acrodynia, and it bears some resemblance to pellagra. Granting that pyridoxine is necessary in human nutrition, and this has not been conclusively proven, its function is not as yet established. Like other better known members of the B complex, pyridoxine has been synthesized and it is available in pure form.

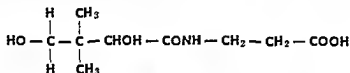
No specific requirements have been established.

### Pantothenic Acid

A deficiency of this member of the vitamin B complex in the diet of chicks results in a dermatitis, incrustations at the corners of the mouth, and skin inflammation. When the diet is lacking in this factor young rats and certain other experimental animals show dermatitis, retarded growth, and graying of the hair. When pantothenic acid is restored to the diet the grayness is replaced by the original color. This has quickened public interest in pantothenic



acid There is, however, no very positive proof that the acid prevents graying of the hair of humans



Pantothenic Acid



Fig 10—Pantothenic Acid (Filtrate Factor) Deficiency of this vitamin causes dermatitis in chickens (left) The chicken heals rapidly following the administration of 10 mg daily of this factor



Fig 11—Vitamin B complex deficiency as manifested in the tongue

RECOMMENDED DAILY DIETARY ALLOWANCES<sup>1</sup> REVISED 1963

Food and Nutrition Board, National Academy of Sciences—  
National Research Council

Designed for the maintenance of good nutrition of practically all  
healthy persons in the U S A

(Allowances are intended for persons normally active in a temperate climate)

	Age <sup>2</sup> Years from to	Weight kg (lbs)	Height cm (in)	Calo- ries	Vitamin A Value I U	Thia- mine mg	Ribo- flavin mg	Niacin Equiv <sup>3</sup> mg	Asc Acid mg	Vita- min D I U
Men	18-35	70 (154)	175 (69)	2900	5000*	1.2	1.7	19	70	
	35-55	70 (154)	175 (69)	2600	5000	1.0	1.6	17	70	
	55-75	70 (154)	175 (69)	2200	5000	0.9	1.3	15	70	
Women	18-35	58 (128)	163 (64)	2100	5000	0.8	1.3	14	70	
	35-55	58 (128)	163 (64)	1900	5000	0.8	1.2	13	70	
	55-75	58 (128)	163 (64)	1600	5000	0.8	1.2	13	70	
	Pregnant (2nd and 3rd trimester)			+ 200	+1000	+0.2	+0.3	+3	+30	400
	Lactating			+1000	+3000	+0.4	+0.8	+7	+30	400
Infants <sup>4</sup>	0- 1	8 (18)		kg x115 ±15	1500	0.4	0.8	6	30	400
Children	1- 3	13 (29)	87 (34)	1300	2000	0.5	0.8	9	40	400
	3- 6	18 (40)	107 (42)	1600	2500	0.6	1.0	11	50	400
	6- 9	24 (53)	124 (49)	2100	3500	0.8	1.3	14	60	400
Boys	9-12	33 (72)	140 (55)	2400	4500	1.0	1.4	16	70	400
	12-15	45 (98)	156 (61)	3000	5000	1.2	1.8	20	80	400
	15-18	61 (134)	172 (68)	3400	5000	1.4	2.0	22	80	400
Girls	9-12	33 (72)	140 (55)	2200	4500	0.9	1.3	15	80	400
	12-15	47 (103)	158 (62)	2500	5000	1.0	1.5	17	80	400
	15-18	53 (117)	163 (64)	2300	5000	0.9	1.3	15	70	400

<sup>1</sup> The allowance levels are intended to cover individual variations among most normal persons as they live in the United States under usual environmental stresses. The recommended allowances can be attained with a variety of common foods providing other nutrients for which human requirements have been less well defined. See text for more detailed discussion of allowances and of nutrients not tabulated.

<sup>2</sup> Entries on lines for age range 18-35 years represent the 25 year age. All other entries represent allowances for the midpoint of the specified age periods, i.e. lines for children 1-3 is for age 2 years (24 months); 3-6 is for age 4½ years (54 months) etc.

<sup>3</sup> Niacin equivalents include dietary sources of the preformed vitamin and the precursor tryptophan. 60 mg tryptophan represents 1 mg niacin.

<sup>4</sup> The calorie and protein allowances per kg for infants are considered to decrease progressively from birth. Allowances for calcium, thiamine, riboflavin and niacin increase proportionately with calories to the maximum values shown.

\* 1000 I U from preformed Vitamin A and 4000 IU from beta-carotene

Pantothenic acid is thought to be essential in human nutrition, possibly in the utilization of other members of the vitamin B complex; it is known to be a part of coenzyme A. The substance is commercially available in the form of the calcium salt. No standards have been proposed. Natural sources of other members of the B complex usually provide pantothenic acid.

### Vitamin B<sub>12</sub> (Cyanocobalamin)

This vitamin was announced in 1948 as a new member of the B complex. The compound has been isolated from commercial liver extracts as a red, crystalline, heat stable substance. It produces a positive hematological response when administered to individuals afflicted with pernicious anemias, nutritional macrocytic anemia, or sprue. Thus the physician now has at his command another agent for treating anemias. An interesting point is that chemical analysis of vitamin B<sub>12</sub> shows the presence of cobalt. Liver, milk, cheese, egg yolks and meats are sources of this vitamin.

In addition to the members of the vitamin B complex just considered, a number of others are known. None of these has as yet been proven essential in the human diet, but certain ones are required by animals. Some of these factors are choline, inositol, biotin, *para* aminobenzoic acid, and folic acid.

### SELF-TESTING QUESTIONS

13. What elements are found in vitamin B which do not appear in vitamin A?
14. In what manner is carbohydrate metabolism disturbed when there is a deficiency of thiamine?
15. State the effects of heat and pH of medium on thiamine.
16. Are members of the vitamin B complex stored in the body? Can you advance a reason for this?
17. Give the chemical names for the better known members of the vitamin B complex.
18. Which members of the vitamin B complex are known to be essential in human nutrition? Give the deficiency symptoms of each.
19. What is the significance of the prefix *ribo-* in the name *riboflavin*?
20. Is it possible to prevent gray hair in humans by the use of vitamins?
21. Which member of the vitamin B complex is associated with the "three d's"?
22. What is cheilosis?
23. Why has pellagra been more prevalent in the southern states than in the northern states of the U S?
24. What is the objection to decortication of cereal grains? Why is it done? Discuss.

### IV. VITAMIN C

Scurvy, the disease which results from an extreme deficiency of vitamin C, has been known for hundreds of years. Beriberi and scurvy in all probability were the first diseases to be attributed to dietary deficiencies. In past centuries sailors on long voyages were

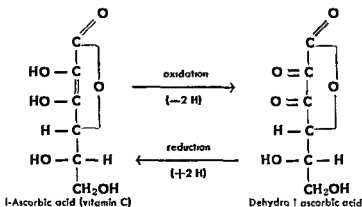
often deprived of fresh fruits and vegetables for weeks at a time, and as a result many were stricken with scurvy and died from its effects. Vitamin C is also known as the anti-scorbutic vitamin, cevitic acid, and l-ascorbic acid, the latter is the chemical name.

### Functions and Deficiency Effects:

The earlier and milder symptoms of ascorbic acid deficiency are general lassitude, soreness of gums, defective teeth, sores in the mouth, etc. These might be called symptoms of subacute or marginal deficiency. In advanced stages there is a reduction in the formation of intercellular substance, a cementing material important in capillary walls, cartilage, and teeth. As a result tissue structure is weakened, blood capillaries tend to hemorrhage, lesions appear in the bone marrow, and teeth may loosen.

It has been proven that man, monkeys, and guinea pigs require l-ascorbic acid. Other animals apparently do not require it, or possibly have the ability to synthesize it.

In point of chemical structure l-ascorbic acid is an oxidized form of a hexose sugar. Like members of the vitamin B complex it is a water-soluble factor. l-Ascorbic acid is an active reducing agent, and as such it is oxidized by loss of hydrogen to give dehydro-l-ascorbic acid. The latter, in turn, is easily reduced to l-ascorbic acid. This oxidation-reduction system of l-ascorbic acid and dehydro-l-ascorbic acid is thought to play a role in reactions which occur in the tissues.



### Sources:

Vitamin C has as its richest natural sources citrus fruits, peppers, raw cabbage, and tomatoes. Little if any is found in dry cereal

grains, meat, and eggs. Cow's milk contains on the average small quantities, with considerable variation depending upon the season of the year. This vitamin becomes especially important in the diets of bottle-fed babies since cow's milk is much poorer than breast milk in l-ascorbic acid. Added to this is the fact that heating milk to sterilize it is somewhat destructive of the vitamin. Orange juice in the infant's diet insures an adequate supply. The nursing mother should likewise be well supplied with l-ascorbic acid. Tests have proven that a substantial percentage of vitamin C is destroyed in cooking, largely the result of the fact that it is easily oxidized. As much as three-fourths of the vitamin C content of fresh vegetables may be destroyed by boiling for one-half hour.



Fig. 12—Vitamin C. Deficiency of this vitamin leads to the development of scurvy, shown at the left. The disease is cured as soon as fresh vegetables and fruits are made a part of the diet (right).

### Assay and Unitage:

Guinea pigs instead of rats serve as test animals in biological assays of l-ascorbic acid. Several methods of chemical analysis have been devised. One of these employs a dye, 2,6-dichlorophenolindophenol, for titrating the vitamin. Methods have been developed for determining the l-ascorbic acid content of the blood and urine. All chemical methods of analysis are dependent upon the fact that l-ascorbic acid is a reducing agent.

The I.U. and U.S.P. unit of l-ascorbic acid are identical, and may be defined as the anti-scorbutic activity of 0.05 milligram of standard l-ascorbic acid. Dietary requirements are usually stated in terms of weight of the acid.

### Requirements:

The recommended daily allowance of vitamin C varies from 30 milligrams for infants to 100 milligrams for adults. Even

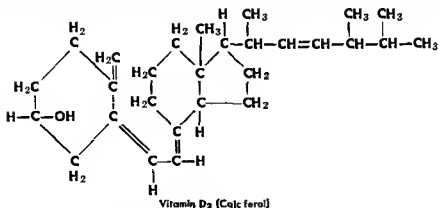
greater amounts are recommended during pregnancy and nursing  
 1 Ascorbic acid is produced commercially and is available in various pharmaceutical preparations

### SELF-TESTING QUESTIONS

- 25 Why were sailors especially susceptible to a vitamin C deficiency? Can you advance a reason for the practice of calling sailors limeys?
- 26 Is the rat a suitable test animal for ascorbic acid studies? Discuss
- 27 In light of the effect of heat on vitamin C how should a housewife modify cooking procedures?
- 28 What rather common type of diet may lead to a marginal scurvy?
- 29 How are infants and growing children protected from vitamin C deficiency? Why is this especially important for bottle fed babies?

### V VITAMIN D

Vitamin D is the factor associated with the disease known as rickets hence the term "anti rachitic" vitamin. There are a number of substances called sterols which possess anti rachitic value, but only two of these warrant consideration. One is ergosterol, a provitamin which under irradiation gives vitamin D<sub>2</sub> and the second is 7 dehydrocholesterol, also a provitamin which upon irradiation provides vitamin D<sub>3</sub>. Vitamins D<sub>2</sub> and D<sub>3</sub> are very similar in chemical structure. Vitamin D<sub>2</sub> is known as calciferol. The structural formula appears below. All members of the vitamin D group are fat soluble.



### Functions and Deficiency Effects

A deficiency of vitamin D in children results in an affliction called rickets. Improper calcification of bones characterizes this

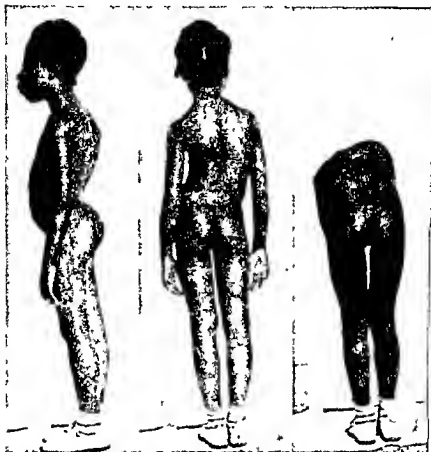


Fig 13—Vitamin D Deficiency. Scoliosis Courtesy, *Therapeutic Notes*

disease. Rachitic bone structures are soft and elastic; this leads to various deformities commonly described as bowlegs, knock-knees, beaded ribs, and pigeon breast. Poor teeth and dental caries can oftentimes be traced to improper calcification arising from insufficient vitamin D.

In adults a deficiency of this vitamin may disturb the calcium and phosphorus metabolism to such a degree that a softening of the bone structures becomes evident. The term osteomalacia applies to such a condition. Blood analyses on rachitic individuals show a low phosphorus but a normal calcium content.

Vitamin D, therefore, is essential for the proper utilization of calcium and phosphorus, elements necessary for bone structures. Merely to provide the body with adequate supplies of minerals which contain these elements is not enough. Vitamin D must also be present for their proper metabolism.

#### Sources:

Ergosterol, provitamin D<sub>2</sub>, is found in ergot and in yeast. It is activated by exposure to ultraviolet light to give vitamin D<sub>2</sub> or calciferol. Irradiated ergosterol is sold under the name viosterol; it provides vitamin D but not vitamin A as is sometimes erroneously supposed. 7-Dehydrocholesterol, provitamin D<sub>3</sub>, is present in the skin, and its irradiation produces active vitamin D<sub>3</sub>.

The best natural sources of vitamin D are the fish liver oils, of which cod liver oil is the best known. Egg yolk and butter are fair sources; however, the majority of natural foods are low or completely lacking in vitamin D.



Fig 14—Vitamin D Deficiency. Rickets. Courtesy, *Therapeutic Notes*



In evaluating this vitamin in human nutrition it must be recognized that bright, direct sunlight is essential for the conversion of the sterol of the skin into an active form, that foods for the most part are lacking in this vitamin and its precursors, and that it is essential for the proper utilization of calcium and phosphorus in building bone structures. Modern living conditions too often deprive us of direct sunlight, and when such is the case supplementary sources of vitamin D should be utilized. This is especially important for infants and children. Some advances in overcoming vitamin D deficiency have been made by the practice of adding irradiated ergosterol to milk and certain other foods. Vitamin D is relatively stable and the usual cooking procedures and storage of foods destroy very little of it.

### Assay and Unitage:

The biological method is the one usually employed for the determination of the vitamin D content of foods. Young rats and chicks are used in the experiments. Rickets is produced in young rats by the use of a so-called rachitic diet, a type which is high in calcium, low in phosphorus, and free from vitamin D, but adequate in all other respects. Rickets appears within a few weeks. The



Fig. 15—The boy with school lunch is in decided contrast to the underprivileged boy, a victim of malnutrition. About how many calories should be provided daily for a growing boy? Courtesy, U S Dept of Agriculture

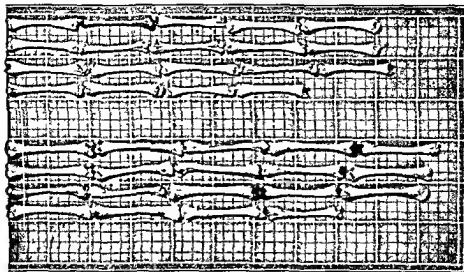


Fig 16—Chickens Are the Largest Consumers of Vitamin D. Notice the difference in bone growth of chicks fed on a control diet (upper group), and those fed with food irradiated to produce Vitamin D. How does vitamin D promote growth? Courtesy, du Pont Company

rachitic rat is then given the food whose vitamin D potency is to be determined, and the calcifying effect on the bones is studied. Such observations may be made by use of the x ray, or by killing the animal and studying the calcification in split sections of the bones.

Another assay procedure is the quantitative determination of the amount of bone ash in bones. Rachitic bones yield considerably less ash than normal bones.

The I.U. of vitamin D is the same as the U.S.P. unit, and is defined as the vitamin D activity of 1.0 milligram of a standard 0.01 per cent solution of irradiated ergosterol (*calciferol*) in olive oil. One gram of cod liver oil contains on the average 100 I.U.

### Requirements:

The recommended daily allowance for children is 400 I.U. This amount is not supplied normally in the diet. The vitamin D requirements for adults have not been established; it is undoubtedly necessary, and when not available through sunshine it should be provided up to 400 I.U. Women during pregnancy and lactation should receive between 400 and 800 I.U. as a daily allowance.

## SELF-TESTING QUESTIONS

- 30 Why is additional vitamin D generally recommended for infants and children but not for adults?
- 31 Name the precursors of the two vitamins D considered here and state how each is activated
- 32 Outline the various symptoms of severe rickets
- 33 How does vitamin D aid in proper mineral metabolism?
- 34 Vitamin D is sometimes called the 'sunshine vitamin'. Discuss
- 35 How is the biological method of vitamin D assay conducted?
- 36 In what important analytical respect do normal and rachitic bones differ?
- 37 Why should an individual's occupation and geographical location be considered in vitamin D requirements?
- 38 Why might activated cod liver oil be preferable to viosterol for youngsters?

## VI. VITAMIN E

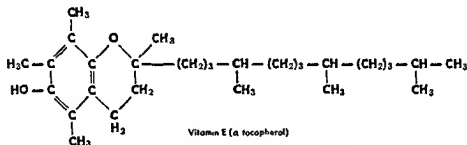
Diets deficient in vitamin E produce sterility in rats. In the male rat sterility is due to degeneration of the germinal epithelium and destruction of spermatozoa. The female rat deprived of this vitamin shows normal conception and formulation of the ovum, however resorption of the fetus occurs. In addition to its part in



Fig. 17—Vitamin E. This vitamin controls the number of babies in a litter of rats.

reproduction there is evidence from work with experimental animals that a lack of vitamin E causes atrophy of the voluntary muscles. This condition is termed muscular dystrophy.

There are at least three closely related substances which exhibit vitamin E activity. These are named  $\alpha$ -,  $\beta$ -, and  $\gamma$ -tocopherol. The first of these,  $\alpha$ -tocopherol, is the most potent and is now available commercially. All are fat-soluble factors.



Vitamin E has a widespread occurrence in the natural foodstuffs. Wheat-germ oil is the best known source; other vegetable oils are excellent. Green leafy vegetables and whole grains are likewise important sources. Vitamin E is highly stable toward heat, acid, and alkali, but it is susceptible to destruction through oxidation. When fats and oils become rancid through oxidation the vitamin E content suffers.

No suitable unit of vitamin E has yet been established, in fact it remains to be proven that it is essential to the reproductive processes in man. Clinical data as yet are not conclusive.

## VII. VITAMIN K

Vitamin K is the anti-hemorrhagic factor. A deficiency of the vitamin leads to a prolonged coagulation time of the blood. As a result there is a tendency for subcutaneous hemorrhage. Prothrombin is required in the normal clotting of blood, and investigations point to the fact that vitamin K is essential for the production of prothrombin.

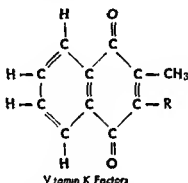
In cases of obstructive jaundice in man there is a lack of bile fluid, and it becomes impossible for vitamin K to be properly absorbed from the intestine. This leads to a reduction in the level of vitamin K in the bloodstream, and surgical operations may prove fatal because of hemorrhage. In such cases physicians administer vitamin K to the patient for several days prior to the operation in order to maintain a safe prothrombin level.

## DATA ON SOME VITAMINS

<i>Names</i>	<i>Deficiency Symptoms</i>	<i>Principal Functions</i>	<i>Best Sources</i>
<b>Vitamin A</b> Anti xerophthalmia vitamin ( $\beta$ -Carotene the chief precursor) Fat-soluble	Eye infections Night blindness Retarded growth Lowered resistance to infections	Maintenance of normal infection resisting tissues Proper functioning of visual purple Promotes growth	Green leafy vegetables Yellow vegetables Fish liver oils Butter
<b>Vitamin B<sub>1</sub></b> Thiamine hydrochloride Anti neuritic vitamin Water-soluble	Digestive disturbances Retarded growth Polyneuritis Beriberi	Stimulates appetite Promotes growth Proper metabolism of carbohydrates Normal gastric and intestinal activity	Yeast Whole cereal grains Pork Liver
<b>Vitamin B<sub>2</sub></b> Riboflavin Vitamin G Water-soluble	Impaired growth Lamitude and weakness Fissures at mouth (cheilosis) Glossitis	Normal growth Prevention of cheilosis	Yeast Whole grains Green leafy vegetables Organ meats (liver etc)
<b>Niacin</b> Nicotinic acid Nicotinamide Anti pellagra vitamin Water-soluble	Gastrointestinal disturbances Mental disturbances Blacktongue (in dogs) Pellagra	Normal functioning of gastrointestinal tract Promotes growth Prevents skin lesions Prevents pellagra	Yeast Glandular meats Fish Green leafy vegetables
<b>Vitamin B<sub>12</sub></b>	Anemia	Produces remission in pernicious anemia	Liver
<b>Vitamin C</b> Ascorbic acid Cevitic acid Anti-scorbutic vitamin Water-soluble	Tenderness of joints Sores in mouth Lowered resistance to infection Scurvy	Proper healing of wounds Normal growth and structure of teeth Prevention of anemia Prevention of scurvy	Citrus fruits Tomatoes Fresh cabbage peppers Fruits, vegetables
<b>Vitamin D</b> Calciferol (D <sub>2</sub> ) Activated 7-dehydrocholesterol (D <sub>3</sub> ) Anti-rachitic vitamin Fat-soluble	Poor assimilation of Ca and P Faulty bone structures Improper calcification Osteomalacia Rickets	Correct utilization of Ca and P in metabolism Prevents faulty tooth structure caries Prevents rickets	Irradiated ergosterol and other sterols Fish liver oils Action of sunlight Vitamin D enriched foods
<b>Vitamin E</b> $\alpha$ Tocopherol Anti-sterility vitamin Fat-soluble	Sterility in rats Placental failures Muscular atrophy in experimental animals	Normal reproduction in rats Prevention of muscular dystrophy in rats	Wheat-germ oil Corn and cottonseed oils Green leafy vegetables
<b>Vitamin K</b> Anti-hemorrhagic vitamin Blood coagulation vitamin Fat-soluble	Prolonged coagulation time for blood Hemorrhage Anemia	Aids in production of prothrombin Normal clotting of blood	Green leafy vegetables Alfalfa Tomatoes

Newborn infants often have a low prothrombin level, and if such is the case, injury at birth may lead to extensive hemorrhage. Here again the physician finds vitamin K valuable, it may be administered to the mother prior to childbirth or to the newborn baby.

There are several related substances which possess vitamin K activity. All are fat soluble. All are derivatives of a structure called 1,4 naphthoquinone. The general formula given here suffices for various substances of vitamin K activity. These factors differ in the nature of the radical  $-R$ .



Vitamin K is of general occurrence in natural foods, green leafy vegetables are outstanding sources. A normal diet provides sufficient vitamin K. However, there is the possibility of faulty absorption when there is a lack of bile fluid or an obstruction of the bile duct.

Vitamin K is heat stable. Its activity is diminished or completely destroyed by strong acids and bases, and by oxidizing agents. Light also has a destructive action.

No standards or recommended allowances have been formulated for vitamin K.

#### SELF-TESTING QUESTIONS

- 39 Discuss vitamin E and vitamin K requirements in human nutrition.
- 40 What is the meaning of *muscle dystrophy*?
- 41 How is it possible for an individual to suffer from lack of vitamin K even though it is adequately supplied in the diet?
- 42 Discuss the applications of vitamin K in medicine.

### VIII VITAMINS IN NUTRITION

There is no disputing the fact that the public annually spends thousands of dollars needlessly on supplementary vitamin preparations. Intensive radio and television advertising and other high

pressure methods have held vitamins before the general public as cures for all varieties of ills, regardless of origin

On the other hand it has been proven conclusively that a number of the vitamins are essential in human nutrition. It is true, also, that under ordinary living conditions the normal adult is provided with sufficient quantities of the necessary vitamins if he wisely selects for himself a varied diet. Authorities agree that infants and children, even under the best dietary conditions, should be provided with supplemental sources of vitamins C and D. When living con-



Fig 18—Fruits and Vegetables Nutrition authorities insist that fruits and vegetables be generously used in the daily diet Why is this? Courtesy, National Dairy Council

ditions are not normal, as in time of war, and when individuals are deprived of an adequate varied diet because of food shortages, poverty, etc., vitamin deficiency symptoms may appear.

Unfortunately, a number of our foods are highly refined. Such a process, as illustrated by the decortication of wheat, removes vitamins and minerals. To remedy this particular situation enriched flour is widely used. Such flour contains added thiamine, riboflavin, niacin, and iron, it is a decided improvement, but even so it does not contain all of the nutritionally valuable factors which were present in the whole grain. The enrichment of whole milk by the addition of vitamin D and of oleomargarine by the addition of vitamin A are additional examples of present day trends in the food industries.

The opinion prevails that America is well fed, yet studies have proven that at least one-third of the population is not receiving a diet which is nutritionally adequate. Every individual owes it to himself to carefully study his dietary habits and assure himself that he is adequately supplied not only with the necessary quantities of carbohydrate, fat, and protein in their proper balance, but also with adequate amounts of those minerals and vitamins which have been proven essential in human nutrition.

## IX. MILK

### As a Food:

Milk is the best and most nearly perfect food, since it contains in an easily digestible and very nourishing form the three nutrients, carbohydrate, fat and protein, most, if not all of the vitamins, a balanced quantity of inorganic salts (especially calcium acid phosphate,  $\text{CaHPO}_4$ ) which are so necessary for the growth of tissues, strong bones and teeth, organic acids, certain nonprotein nitrogenous constituents, and a number of active enzymes and bacteria.

Milk, however, has some deficiency, otherwise it would be considered a perfect food. It is a very dilute food (87 per cent water) with a low content of vitamins B, C, D, and a low content of iron, the latter element being essential to the formation of hemoglobin.

Milk is amphoteric in reaction, though normally it is slightly acid (pH 6.6 to 6.9).

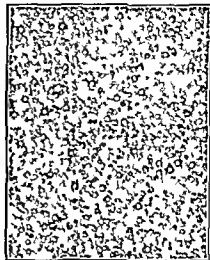
### Composition:

The constituents of the milks of all species are the same, but not in the same percentage, each species developing a milk particularly





A



B

Fig 19—Heat Changes the Size of Fat Globules in Milk. (A) shows the fat globules in bottled milk and (B) shows them in evaporated milk (Magnification 1000 times for both.) What inferences can be drawn from these pictures? Courtesy Evaporated Milk Association



Fig 20—Milk made the difference. Why is ordinary cow's milk not a perfect food?

adapted for the growth of its own kind. In fact, the composition varies directly with the length of the time required for the development of that species. Thus infants grow slowly and double their

weight in 180 days, cows in 47 days, cats in 9 days, and rabbits in 6 days. It follows, then, that cow's milk may be good, but not the best, milk for infants. For this brief treatise, only human, cow, goat, and mare's milk will be considered, their relative composition being shown in the following table.

<i>Constituent</i>	<i>Human</i>	<i>Cow</i>	<i>Goat</i>	<i>Mare</i>
Water	87.5	87.0	87.0	87.5
Carbohydrate (lactose)	6.0 to 7.5	4.5 to 5.5	4.4	6.89
Fat	2.0 to 4.0	2.0 to 5.0	4.1	1.17
Protein (casein, lactalbumin, lactoglobulin)	0.7 to 1.5	2.5 to 4.0	3.7	1.84
Ash (salts of P, Ca, Mg, K, Na, Cl, etc.)	0.3 to 0.15	0.6 to 0.7	0.9	0.3

A comparison of the composition of the different milks shows that mare's milk more closely resembles human milk than does cow's milk, and consequently is an excellent substitute for mother's milk. Goat's milk is somewhat similar to cow's milk.

The lactose of milk sugar is derived from blood sugar (glucose). The fats are derived from the phospholipids of the blood and are mostly composed of palmitin and olein, with smaller amounts of stearin and myristin, and still smaller amounts of the glycerides of lower fatty acids (butyric, caproic, etc.) Other lipids presented in traces are lecithin, cholesterol. The yellow compound is lactochrome. The proteins are derived from the amino acids of the blood, and are mostly composed of casein (80 per cent), the remainder being lactalbumin and lactoglobulin. The salts and remaining constituents are also derived from the blood.

Milk is not to be considered as filtered fluid from the blood plasma. It is a secretion containing the specific compounds lactose and casein formed in the glands, although many of its constituents (vitamins, uric acid, urea, etc.) must have dialyzed from blood plasma. After delivery and for many days the mammary glands secrete a yellowish, alkaline fluid called *colostrum*, which acts as a purgative on the newly born infant. Such a milk has a high content of total solids, the chief constituent of which is albumin.

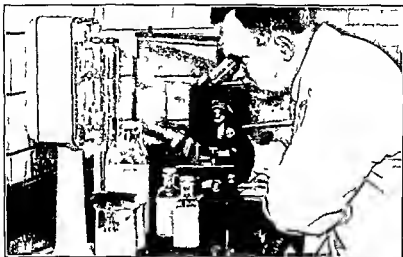


Fig. 21—A Milk Laboratory. Trained chemists and bacteriologists analyze milk to meet specified standards. What advantages has this laboratory? Courtesy, Supplee-Seeltest, Philadelphia.

The composition of milk is changed somewhat by *variations* in diet, but the flow and yield are influenced by such factors as diet, age, nerve conditions, etc.

### Modified Milk:

Milk may be modified to resemble human milk, but it is never "just as good." From the preceding table it is evident that *cow's milk is high in protein but low in sugar as compared with human milk*. By diluting cow's milk and adding sugar (preferably lactose or Dextri-maltose) a satisfactory mixture of practically the same composition as human milk is obtained (Fig. 22). Too much added sugar (over 7 per cent), although fattening, may cause gas and colic and lead to serious trouble. Unless cow's milk is diluted, the high protein content may cause indigestion and colic. Too much fat also leads to various disturbances. Goat's milk is somewhat richer in fat and contains slightly more salts than either human or cow's milk, and it, like cow's milk, contains less lactose than human milk. Since milk has some nutritional deficiencies it is essential that the growing infant within six or seven weeks after birth be supplied with orange or tomato juice as a vitamin C corrective, and a week or so later with cod liver oil or exposure to direct sunlight (ultraviolet light) for vitamin D deficiency. Iron deficiency will be

automatically taken care of months later when the milk diet is being supplemented with egg concoctions and purees of green vegetables. A recent practice is the addition of minerals and vitamins to provide a fortified milk.

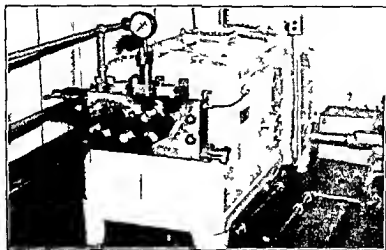


Fig 22—Homogenizing Machine. Since milk is somewhat modified by the ration of the cow, many milk concerns are meeting the demands of physicians for modified milks such as vitamin milk, iodized milk, soft curd milk, homogenized milk, etc. How may the vitamin content of a milk differ in the winter from that in the summer? Courtesy: Supples Sealtest Philadelphia.

## Pasteurization

Since cow's milk is liable to become contaminated with the different pathogenic bacteria which produce tuberculosis, typhoid fever, dysentery, and other serious diseases, milk is pasteurized. Pasteurization is a process of heating milk to  $63^{\circ}\text{C}$ , for 30 minutes, then quickly cooling it, and protecting it from contact with the air (Fig 23). Milk so treated is free from all disease-producing organisms and is just as digestible and nutritious as raw milk, but it has a slightly different taste because of formation of a volatile sulfide (probably  $\text{H}_2\text{S}$ ) from partly decomposed proteins, and contains less than half the antiscorbutic vitamin C normally present. Since vitamin C in raw milk is not present in sufficient quantities, it follows that this is not such a serious loss. The deficiency of vitamin C, as mentioned, may be provided for by orange or tomato juice.

Since pasteurization destroys some of the vitamin potency of milk, health authorities have allowed raw milk to be sold under

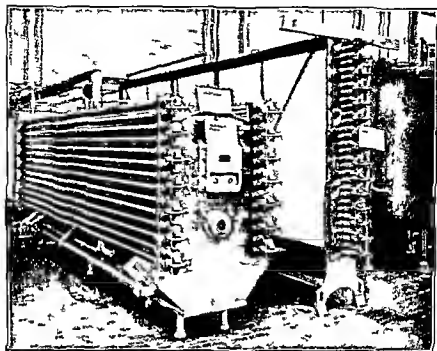


Fig 23—Guardians of Public Health Milk in nickel lined vats is pasteurized by heating with hot water at  $63^{\circ}\text{C}$  for 30 minutes. There without contact with air it is quickly cooled in a series of pipes. What is the advantage of the relatively low temperature upon pathogens present in the milk? Courtesy Bowman Dairy Co

certain restriction as *certified milk*. Such a milk is produced from disease free cows, the milk being handled under rigid sanitary conditions, and when sold must not show a count over 10 000 bacteria per ml.

### Lactic Acid Milk

Upon standing, milk sours and curdles as the result of lactic acid fermentation of the lactose present



At pH 4.7 its isoelectric point the casein precipitates and the milk is said to curdle. The curdling of milk may also be brought about by the addition of rennin in the form of rennet as obtained from the lining of calves' stomachs. The rennin changes soluble

calcium caseinate into insoluble calcium paracaseinate. In precipitating casein by either acids or rennin, some fat and traces of other constituents are removed from the milk. Such a mixture is used to make cheese, the flavor and kind depending upon the type of organism present during the fermenting or ripening process. The liquid surrounding the curd is known as whey. Lactic acid milk, such as buttermilk and acidophilus milk, is considered much more digestible than untreated milk. Furthermore, it is interesting to learn that pathogenic bacteria will not grow in sour milk. So it is



Fig. 24—Milk and Its Products. Which food pictured would you expect to be highest in fat content? in protein content? in water content? Courtesy of National Dairy Council.

that nature comes to man's assistance in protecting milk, the most important of all our foods. Such bacteria change the intestinal flora by forming an acid medium which is unfavorable for the growth of putrefying and fermentative bacteria.

### Fuel Value

Milk is a good fuel because it contains fat and sugar. One quart of milk yields 675 Calories, an amount sufficiently ample to supply

Child, 1 year old with two thirds of total calories required daily

Child, 5 years old, with one half of total calories required daily

Boy, 10 years old, with one third of total calories required daily

Man, 21 years old, with one fourth of total calories required daily

One glass of milk yields approximately 100 Calories, which is equivalent in fuel value to any of the following

2 eggs (large)

2 potatoes (medium)

2 slices of bread

1 large serving of lean meat

From a financial standpoint, the amount of energy from a quart of milk is far in excess of that obtained from the same amount of money expended for meat and eggs. Besides being valuable as fuel to keep the body warm, we must not lose sight of the fact that milk also repairs tissues, promotes growth, and builds bone.

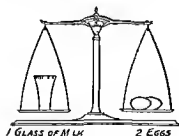


Fig. 25—Economic Value of Milk. Milk is almost an ideal food. What prevents it from being a perfect food?

### Protein Content

It has already been mentioned that the most important difference between cow's milk and human milk is the high protein content of cow's milk. When milk enters the stomach, rennin, the gastric juice ferment, hydrolyzes the casein (85 per cent of the protein of

milk) into soluble paracasein, which combines with the calcium salts to form an insoluble curd, called paracaseinate. Provided the milk is drunk slowly, the curd will be soft and in a finely divided state, in which form it can easily be digested by pepsin. Since the casein of human milk is of a still more flocculent state it should be considered more digestible.

Cereal proteins are very low in lysine and tryptophan, two very important amino acids, which are absolutely essential for growth. According to the findings of Rose\* there are at least eight amino acids which are essential to maintain the body's growth and repair: lysine, tryptophan, phenylalanine, leucine, isoleucine, threonine, methionine, and valine.

Foods which contain the essential amino acids are almonds, cheese, eggs, lean meat, milk and gluten of corn. The addition of milk to cereal foods aids greatly in nutrition.

### Mineral Content

Milk contains a well-balanced quantity of inorganic salts, all that are needed in nutrition. It contains a very plentiful supply of calcium and phosphorus compounds which are needed for growing strong bones and teeth. A glance at the following illustration shows the amount of lime in various foods.

<i>Food</i>	<i>Length of line gives proportional amount of lime</i>
1 cup of milk	_____
1 cup of carrots	_____
1 egg	_____
2 slices of bread	—

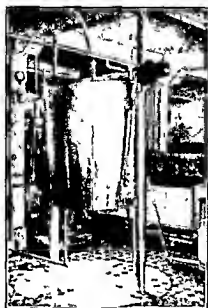
Although there is a low content of iron, still it is in sufficient quantity and suitable form to supply amply the nutrition requirements.

### Vitamin Content

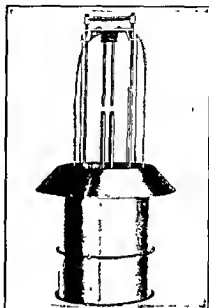
Milk contains most, if not all of the vitamins, being especially rich in vitamin A and vitamin B<sub>2</sub>, the ones most important for normal growth and for preventing certain deficiency diseases. But for the fact that milk is low in vitamin B<sub>1</sub> (antineuritic), C (antiscorbutic), D (antirachitic), in iron, in hemoglobin forming and reproduction forming substances, milk would be a perfect food.

\* W. C. Rose, *Chem and Eng News* vol 30 p 2298 1952





A



B

Fig. 26—Irradiating Milk with the Ultraviolet Ray. Provitamin D, naturally present in milk, is instantly converted into vitamin D, the antirachitic vitamin, by exposing it a few seconds to the rays from an electric arc (B) on a rapidly moving film. By what other means can milk be made to contain a high vitamin D content? Courtesy, Belle-Vernon Co

In conclusion, it is very evident that milk has practically everything needed in the diet, all the necessary substances for nutrition. The dietary rule of a quart of milk each day for every child is much more than a precept based on individual opinions or drawn by analogy from the results of feeding experiments with lower animals; it now rests on scientific evidence obtained by extensive and intensive experiments directly upon the children themselves.

As a rule, children must have one quart of milk, and adults should have one pint of milk daily.

### SELF-TESTING QUESTIONS

43. What materials are present in milk that make it a desirable food?
44. What keeps milk from being called a perfect food?
45. In what two noticeable respects does human milk differ from cow's milk?
46. What is the function of colostrum?

- 47 How may cow's milk be modified so as to compare favorably with human milk?
48. Too much sugar and protein in milk may cause what trouble?
- 49 How are the nutritional deficiencies of milk supplied in infant feeding?
- 50 How is milk pasteurized and how does pasteurization affect its vitamin content?
- 51 Milk may be curdled by what two substances?
- 52 Why is buttermilk or acidophilus milk considered very digestible?
- 53 How does milk compare with other foods as a source of energy?
- 54 What two important amino acids occur in milk, and are essential for growth?
- 55 What compounds occurring in milk are essential for growing bones and teeth?
- 56 What are the two most important vitamins in milk, and what are their functions?

## SUGGESTED ACTIVITIES

### I. THOUGHT PROVOKING QUESTIONS

- 1 Advance an explanation for the fact that the fat soluble vitamins are stored for a time in the body, while the water soluble vitamins are not
- 2 Which of the vitamins are most likely to be inadequately supplied in the diet? How can this be easily remedied?
- 3 Which vitamins are especially important in the diets of babies and children? What two items in the infant's diet will supply these?
- 4 What is the function of the so-called protective foods?
- 5 Discuss the effect of pH of medium on vitamin stability. Comment on the practice of adding soda in cooking certain green vegetables to preserve the color.
- 6 Cite several cases where the vitamin is known to play a direct part in metabolism.
- 7 Do you feel from observations that the average citizen of this country enjoys an adequate diet?
- 8 Can you suggest a reason why niacin has been substituted as a name for nicotinic acid?
- 9 What part of the sunlight is effective in activating the sterol in the skin? Why is direct exposure to sunlight necessary?
- 10 How can you account for the fact that the vitamin C content of milk varies considerably with the season of the year?
- 11 What advances have been made in the food industries to provide vitamins in nutrition?
- 12 Discuss milk as a source of vitamins.
- 13 Why is milk called our most perfect food? Does it have any deficiencies?
- 14 How are the disadvantages of milk as a food corrected?
- 15 How do cow's milk and goat's milk differ from human milk?
- 16 How are cow's and goat's milk modified when used as food for babies?

- 17 What is the effect of the *Lactobacillus acidophilus* on the intestinal flora?
- 18 What factors will increase lactation? Decrease?

## II VOCABULARY TESTING OF NEW TERMS

polyneuritis	anti neuritic	cheilosis
beriberi	microgram	keratitis
decortication	anti rachitic	dysirophy
vitamin	ergosterol	precursor
carotene	acrodynia	nyctalopia
hypovitaminosis	viosterol	provitamin
avitaminosis	calciferol	ribose
anti xerophthalmic	irradiation	anti scorbutic

## III TOPICS FOR ORAL OR WRITTEN REPORTS

- 1 Diseases Due to Vitamin Deficiencies
- 2 Recommended Vitamin Allowances in the Diet
- 3 The Use of Supplementary Vitamin Preparations
- 4 Cow s Milk in Infant Feeding

## LABORATORY CHEMISTRY

Laboratory exercises for this chapter will be found on page 766

## REVIEW OF DEFINITIONS

## CHAPTERS XVIII THROUGH XXIII

The following terms are important in the study of chemistry. A mastery of them will help one build a scientific vocabulary that will be invaluable in future study or reading.

*acetonuria* (as e-to nu ri a) A condition marked by the presence of acetone and acetone bodies in the urine

*albuminuria* (al hu min u re-a) Albumin in the urine

*alkaline tide* An alkaline condition in the urine following meals due to the withdrawal of hydrogen ions to form the hydrochloric acid in the stomach

*amyllopsin* (am il op sin) The starch hydrolyzing enzyme of the pancreatic juice

*anabolism* (an ab o lizm) Constructive metabolism. The opposite of *catabolism*

*antienzyme* A substance that inactivates an enzyme

EXAMPLE  $\text{HgCl}_2$

*antiketogenic* Substances that prevent acidosis

*anuria* (an u ri a) Refers to the condition when scarcely any urine is secreted

*ascorbic acid* (as kor'vik) Vitamin C

*avitaminosis* (a vi ta min o sis) A pathological condition due to the lack of a vitamin.

EXAMPLE Rickets

*basal metabolism* The minimum amount of energy required to maintain life when the body is at rest and without food

*bile* The secretion of the liver that aids in digestion and absorption of fats in the intestine

*blood* A circulating tissue existing in a closed system of tubes which branch off to every cell

*calciferol* A crystalline compound that is isomeric to ergosterol and influences calcium metabolism

*carbohydrate tolerance* The capacity of the body to oxidize or store glucose

*carotene* (cär o ten) A yellow compound in plants from which vitamin A is synthesized by the animal organism

*casts* Cylindrical formations of proteins that are discharged into the urine from the kidney tubules

**catabolism** *Destructive metabolism* Opposite of *anabolism*

**cholesterol** (kol-es ter-ol) A bile constituent which assists in fat absorption

**chyluria** (ki lu re-a) The presence of chyle in the urine

**coenzyme** Enzyme activator

**condensation** Reactions between like or unlike molecules with or without the loss of water

EXAMPLE Formaldehyde plus phenol to form resin

**deamination** (de am in s shun) A process involving the splitting off of the nitrogen of the amino group into ammonia

**digestion** The breaking down of complex bodies into simple soluble ones which the body can absorb and use

**enterokinase** (en ter o ki'nas) An enzyme which activates trypsinogen

**enzymes** (en zimes) Catalysts produced in life processes

EXAMPLE Pepsin

**erpsin** The protein hydrolyzing enzyme of the intestinal juice

**ergosterol** (ar gos te rol) The substance which upon exposure to ultraviolet rays changes to vitamin D

**erythrocytes** (er ith ro sites) Red corpuscles

**hematuria** (hem at u re a) Blood in the urine

**hemoglobinuria** (hem o-glo-hin u re-a) Hemoglobin in the urine

**heparin** An antiprothrombin

**hirudin** A commercial anticoagulant extract from leeches

**hormones** Internal secretions of the endocrine glands which stimulate certain tissues or organs

EXAMPLE Secretion stimulates the pancreatic cells to cause a flow of pancreatic juice

**inverting enzyme** The sucrose hydrolyzing enzyme in the intestinal juice

**irradiated** Pertaining to ultraviolet radiations of the skin or of foods

**isoagglutinins** Antibodies which agglutinate the blood cells of those of the same species

**ketogenic** (ke-to jen ik) Substances which may produce acidosis or ketosis

**ketosis** (ke-to sis) A condition of acidosis

**leukemia** (lu ks me-a) Pathological condition of the blood when it contains an abnormal number of white blood cells

- leukocytes* (lu'ko sites) White blood corpuscles
- lymph* An alkaline fluid, colorless, in the lymphatics and bathing each cell
- metabolism* The chemical and energy changes taking place in tissues They may be anabolic or catabolic
- oliguria* (ol ig u're-a) A scanty secretion of urine
- pepsin* The protein hydrolyzing enzyme of the gastric juice
- plasma* The fluid part of blood and lymph
- platelets* Round, colorless discs in the blood which assist in the change of soluble fibrinogen into insoluble fibrin to form the blood clot
- polyuria* (pol e-u re-a) Excessive secretion of urine
- prothrombin* A zymogen which combines with the calcium salts to form thrombin, an enzyme
- ptyalin* (ti al in) The starch hydrolyzing enzyme of the saliva
- pyuria* (pi u re-a) Pus in the urine
- rennin* The enzyme that hydrolyzes casein of milk into paracaseinate
- secretin* A hormone which stimulates the pancreas
- serum* The clear yellow liquid left after the removal of fibrinogen from the plasma
- steapsin* The fat hydrolyzing enzyme of the pancreatic juice
- syneresis* (sin-er e-sis) A shrinkage exhibited by fibrin and other colloidal gels
- threshold point* The point of concentration when glucose begins to pass from the blood into the urine
- thrombin* An enzyme which changes soluble fibrinogen into insoluble fibrin
- thromboplastin* A factor from damaged platelets and tissue which initiates blood clotting
- trypsin* A protein hydrolyzing enzyme of the pancreatic juice
- urinary calculi* Compact masses of insoluble mineral salts in the urinary tract
- vitamins* Substances that are essential for normal nutrition
- zymogen* The inactive state of an enzyme, a proenzyme
- EXAMPLE Pepsinogen.

## **PART IV**

## **APPENDIX**

### **SOME ADDED INFORMATION FOR REFERENCE WORK**

#### **CONTENTS**

I	Antidotes for Some Common Poisons	620
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## I ANTIDOTES FOR SOME COMMON POISONS

<i>Name</i>	<i>Antidote or Treatment</i>
Acids (mineral)	Milk of magnesia limewater in milk soapsuds baking soda Do not use an emetic
Alkalies (caustic)	Citrus juices vinegar buttermilk Demulcents Do not use an emetic
Alkaloids	Strong coffee for morphine and opium otherwise strong tea
Chloroform ether	—cold water on head and chest Artificial respiration
Phenol	Glass of 50 per cent alcoholic liquid Remove by emetic (mustard) Epsom salts egg white milk
Salts of heavy metals (As Cu Pb Hg Ag Zn)	Egg white milk Remove by emetic
Unknown poison	One spoonful of two parts powdered charcoal one part magnesium oxide one part tannic acid Keep dry until ready for use and then use one heaping teaspoonful in a glass of warm water

## II ANTISEPTICS AND DISINFECTANTS

Antiseptics are chemicals which check the growth of bacteria, while disinfectants destroy the bacteria. This classification or division of such chemicals into antiseptics and disinfectants depends not so much upon the actual substance used as it does upon the strength of the solution. A brief consideration of some common examples is listed as follows:



## ANTISEPTICS

<i>Used for</i>	<i>Chemicals</i>	<i>Uses</i>
Hands	Bichloride of mercury ( <i>mercuric chloride</i> )	One tablet ( $7\frac{1}{2}$ grain) in one pint of water makes a 1 : 1000 solution, which is chiefly used on the hands previous to the performance of an operation. Continued use irritates the skin. It is not used on surgical instruments as it <i>corrodes metal</i> .
	Alcohol (ethyl alcohol)	A 50 to 70 per cent solution will penetrate bacteria, but stronger solutions are not so active. So called green soap owes its germicidal action in part to the alcohol (43 per cent) contained in it. Alcohol coagulates and precipitates proteins.
Skin	Sulfur	Used as an ointment to check the growth of bacteria, and to destroy parasites as in scabies.
	Ichthyol	It is an antiseptic in various skin diseases to relieve itching and to soften the skin.
	Soapsuds	Ordinary lather destroys most germs, after thorough scrubbing and then rinsing under running water.
Wounds and ulcers	Hypochlorite solutions	Dakin's solution contains 0.45 to 0.50 per cent sodium hypochlorite. Free chlorine is liberated to combine with the $\text{NH}_2$ radical of the proteins in the tissues to form chloramine which as an antiseptic is about 15 times as effective as phenol, and is not injurious to the tissues.
	Potassium permanganate	It is an oxidizing disinfectant in 1 to 3 per cent solutions for wounds and in 1 : 1000 to 1 : 5000 solutions for gargles and douches.

## ANTISEPTICS (continued)

<i>Used for</i>	<i>Chemicals</i>	<i>Uses</i>
Wounds and ulcers	Iodoform	Mostly used in gauze soaked with a 5 to 10 per cent solution of iodoform. Not commonly used any more.
	Picric and tannic acids	Used chiefly in treatment of burns or scalds. Stops bleeding.
	Phenyl mercuric nitrate	Effective against many skin infections. Is not poisonous, destructive, or irritative to tissues or open wounds. Noncorrosive to surgical instruments. Is many times more powerful than bichloride of mercury, Mercurochrome, or phenol.
Mucous membranes	Boric acid	A 2 to 4 per cent solution is used in eyes, nose, or other sensitive membranes without producing any irritation.
	Compound sodium borate solution (Dobell's solution)	A 1½ per cent sodium borate, phenol, sodium bicarbonate, glycerin and water solution mostly used as an alkaline gargle and as an antiseptic nasal douches.
	Silver nitrate	A 1 per cent solution (followed by physiological saline solution) in the eye of the newborn to prevent gonorrheal infection. In stronger solutions (5 to 10 per cent) it is very destructive to the tissues.
	Mild protein silver (Argyrol)	As a colloidal solution of silver and albumin it is used in 10 to 25 per cent solutions for antiseptic and astringent purposes. Less irritating than silver nitrate.

## DISINFECTANTS

<i>Used for</i>	<i>Chemicals</i>	<i>Uses</i>
Purifying air in rooms Preserving tissues	Formaldehyde (gas)	A 40 per cent solution of formaldehyde gas is called by the trade name 'formalin' A 4 per cent solution preserves tissues a 1 to 2 per cent solution disinfects instruments
	Sulfur dioxide	Formed by burning sulfur Disinfects but will bleach colored fabrics
Purifying the air and certain solutions	Chlorine	This gas in the presence of moisture is a powerful disinfectant It is used mostly as chlorinated lime to disinfect stools and urine and also to remove odors. Used commercially to purify drinking water Oxidizes bacteria directly, or combines with the amino group ( $-NH_2$ ) of bacterial cell to form chloramine ( $NH_2Cl$ ) which kills the bacteria by oxidation
Sinks etc	Phenol (carboic acid)	Two to five per cent solutions are fatal to all bacteria Concentrated solutions are corrosive
	Cresols	Generally prepared as emulsions or soapy solutions (common trade name of Lysol) They are more powerful than phenol
Skin	Iodine	A $2\frac{1}{2}$ to $3\frac{1}{2}$ per cent solution of iodine in alcohol (or in water $+KI$ ) is used to disinfect the skin before an operation Disinfection is due to oxidation and precipitation of protein
	Merthiolate	An organic combination containing about 50 per cent mercury, and less toxic than bichloride of mercury, used mostly in solutions of 1 1000 to 1 2000
	Metaphen	A yellow odorless powder containing about 56 per cent mercury in organic combination more powerful than bichloride used on skin 1 200 and for irrigations 1 2500 to 1 10 000
Wounds	Merbromin (Mercurochrome)	Two per cent solution is used for surface wounds and infections Not very valuable

### III. METHODS OF MEASUREMENT

#### 1. Metric Measurement Based on Decimals

Up to the time of the French Revolution, there was much confusion arising from the use of different standards in different localities to measure length, volume, and weight. Accordingly, a commission, appointed by National Assembly of France, devised a uniform and unchangeable standard, which was called the *metric system*. This system is used almost exclusively in every civilized country excepting the English speaking countries, and even there it is used for scientific measurement. Its great advantage is in being a decimal system, in which its divisions and multiples are in ratio of tens, and therefore easy to work with.

The practical use of the metric system in the hospital is its employment in connection with medication and treatments, apparatus and instruments, laboratory work and metabolic work.

#### METRIC UNITS OF LENGTH, VOLUME, AND WEIGHT

##### The Meter Is the Unit of Length

1 meter (m.)	=	10 decimeters (dm.)
1 decimeter	=	10 centimeters (cm.)
1 centimeter	=	10 millimeters (mm.)
1 millimeter	=	1000 microns ( $\mu$ )
1000 meters	=	1 kilometer (km.)

##### The Liter Is the Unit of Volume

1 liter (l.)	=	1000 milliliters (ml.)
--------------	---	------------------------

NOTE: ml is frequently written as cc (cubic centimeter)

##### The Kilogram Is the Unit of Weight (Mass)

1 kilogram (kg.)	=	1000 grams (Gm.)
1 gram	=	1000 milligrams (mg.)

Remember 1 kilogram = 1000 Gm

1 gram = 1000 mg

1 liter = 1000 ml, or cc

#### 2. Metric-English Conversion Factors

To Change	To	Multiply by
meter	inch	39.37
inch	centimeter	2.54
liter	quart (liquid)	1.057
quart (liquid)	liter	0.946
kilograms	pound	2.205
pound	gram	453.59
gram	gram	15.432
ounce (fluid)	milliliter	29.57
ounce (avoir)	grams	28.35
gallon	liters	3.785

### 3. Apothecary System and Metric Equivalent:

#### Apothecary's System

60 grains (gr) or minims (℥)	≈ 1 dram (℥)
8 drams	≈ 1 ounce (℥)
12 ounces	≈ 1 pound (lb)
	or
16 ounces (fluid)	≈ 1 pint (O)

#### Metric-Apothecary Equivalent (Approximately)

1 gram	= 15 gr	1 ounce	= 30 Gm
1 cubic centimeter	= ℥ xv	1 fluidounce	= 30 cc.
1 fluidram	= 4 cc	1 quart	= 1 l.
1 dram	= 4 Gm	1 grain (¼ Gm)	= 0.064 Gm

#### Equivalents

<i>Metric</i>	<i>Apothecary</i>	<i>Household</i>
4 cc ≈ 4 Gm	℥ 60 ≈ gr 60 ≈ 31	1 t = ½ T = 60 gtt

### 4. Household Measures:

#### Household Measures

60 drops (gtt)	= 1 teaspoonful (t.)
3 teaspoonfuls	≈ 1 tablespoonful (T)
2 tablespoonfuls	= 1 fluidounce
6 fluidounces	= 1 cupful
8 fluidounces	≈ 1 glassful

#### Approximate Equivalents

60 gtt	= 1 teaspoonful
	≈ 4 cc or ml.
	≈ 60 minims
	≈ 60 grains
	≈ 1 dram
	≈ ¼ ounce

### 5. Convenient Relations:

1 ml of water at 4° weighs 1 Gm  
 5-cent piece weighs about 5 Gm  
 1 dime weighs about 2.5 Gm  
 1 dime is about 1 mm thick

1 quart is almost a liter  
 1 test tube, 6 x ¾ holds about 18 ml.  
 1 ml is about 15 drops

## IV. TEMPERATURES

### 1. Temperature Scales:

The only difference between the Fahrenheit (F) or the ordinarily used thermometer in our homes and the centigrade (C) or scientifically used thermometer is the manner in which they are graduated. The temperatures at which chemically pure water freezes and boils are taken as fixed points on both scales when the barometric pressure is 760 mm. Examination of the figure shows the freezing point, boiling point, and the relation between them. A simple method for conversion from one to another follows:

To change Fahrenheit temperature to centigrade Add 40, multiply by  $5/9$ , subtract 40

To change centigrade to Fahrenheit Add 40, multiply by  $9/5$ , subtract 40

## 2. Some Important Centigrade Temperatures:

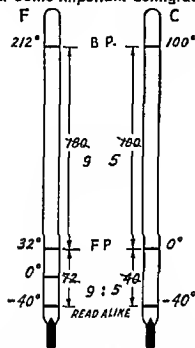


Fig 1—In the three points of equivalence the two intervals are in the ratio of 9:5

-273.13	Absolute zero
-268.9	Helium boils
-252.8	Hydrogen boils
-195.8	Nitrogen boils
-183	Oxygen boils
-112	Grain alcohol freezes
-78.5	Carbon dioxide sublimates
-38.8	Mercury freezes
-33.4	Ammonia boils
-10	Sulfur dioxide boils
0	Ice melts (water freezes)
20	Room temperature (average)
37	Temperature of body (normal)
60	Wood & metal melts
78.4	Grain alcohol boils
100	Water boils
170	Sugar melts
231.9	Tin melts
271.0	Bismuth melts
327.5	Lead melts
658.7	Aluminum melts
1063	Gold melts
1083	Copper melts
1535	Iron melts
1600±	Sand melts
2500±	Temp oxy hydrogen flame
2700±	Temp oxy acetylene flame
4000±	Temp electric arc
6000±	Temp sun's surface

## V. SOME QUALITATIVE TESTS

### 1. Borax Bead Tests:

When a clear borax bead, made by fusing borax on the end of a platinum wire, is touched to a speck of certain compounds and reheated either in the oxidizing (outer) flame or in the reducing (inner) flame, the following colors are produced

Metal	Oxidizing Flame	Reducing Flame	Metal	Oxidizing Flame	Reducing Flame
Chromium	Green	Green	Manganese	Violet	Colorless
Cobalt	Blue	Blue	Nickel	Brown	Colorless or turbid
Iron	Yellow	Green			

## 2. Cobalt Nitrate Tests:

When a substance is intensely heated on a charcoal block before and after being moistened with a dilute solution of cobalt nitrate, the following colors are produced

<i>Metal</i>	<i>Color</i>
Aluminum Magnesium Zinc	Blue when Al compound is infusible Pale pink a somewhat unsatisfactory test Green

## 3. Common Acid Radical Tests:

<i>To Test for</i>	<i>Add</i>	<i>Result</i>
Bromide Carbonate	Cl <sub>2</sub> water + CS <sub>2</sub> HCl	CS <sub>2</sub> is colored yellow to red Gas, CO <sub>2</sub> , which in turn forms a white ppt (CaCO <sub>3</sub> ) with limewater
Chloride	AgNO <sub>3</sub>	White ppt AgCl, insoluble in HNO <sub>3</sub>
Iodide	Cl <sub>2</sub> water + CS <sub>2</sub>	CS <sub>2</sub> is colored violet
Nitrate	FeSO <sub>4</sub> (sat) + conc H <sub>2</sub> SO <sub>4</sub>	Brown ring forms
Phosphate	Ammonium molybdate solution and warm	Yellow ppt insoluble in HNO <sub>3</sub>
Sulfate	BaCl <sub>2</sub>	White ppt BaSO <sub>4</sub> insoluble in HCl or HNO <sub>3</sub>
Sulfide	HCl	Gas, H <sub>2</sub> S, which turns lead acetate paper black (PbS)
Sulfite	HCl	Gas SO <sub>2</sub> , which decolorizes KMnO <sub>4</sub> solution

## 4. Flame Tests:

Compounds of the following metals held in the flame on a platinum wire show the following colors

<i>Metal</i>	<i>Color</i>	<i>Metal</i>	<i>Color</i>
Barium	Yellowish green	Potassium	Violet
Calcium	Orange red	Sodium	Yellow
Copper	Emerald green	Strontium	Red (crimson)
Lithium	Red (carmine)		

## 5. Tests for Combustible Gases:

H <sub>2</sub>	Begins to burn with slight explosion and an almost invisible flame, water forming from the combustion may be condensed on a cold glass surface
CO	Burns with pale blue flame to form carbon dioxide which clouds limewater
CH <sub>4</sub>	Burns with a luminous flame to form carbon dioxide and water
C <sub>2</sub> H <sub>4</sub>	Odor, burns with smoky flame, decolorizes bromine water
C <sub>2</sub> H <sub>2</sub>	Odor, burns with very sooty flame decolorizes bromine water
H <sub>2</sub> S	Odor of spoiled eggs, burns with bluish flame to form sulfur dioxide, darkens moist lead acetate paper

## 6. Tests for Noncombustible Gases:

HCl	Sharp pungent odor, fumes in moist air, and with ammonia forms white cloud (NH <sub>4</sub> Cl), turns moist litmus paper red
SO <sub>2</sub>	Odor of burnt matches, decolorizes potassium permanganate solution
Cl <sub>2</sub>	Sharp odor, greenish yellow color bleaches moist litmus paper
CO <sub>2</sub>	Colorless and odorless forms white precipitate with limewater
NO <sub>2</sub>	Sickening odor, brown color, very soluble
N <sub>2</sub>	Reacts with hot magnesium to form a nitride which with hot water yields ammonia
NH <sub>3</sub>	Sharp penetrating odor, turns moist litmus paper blue, with hydrogen chloride forms white fumes of ammonium chloride
O <sub>2</sub>	Odorless, causes glowing splint to blaze, reacts with nitric oxide to form brown nitrogen dioxide
N <sub>2</sub> O	Sweetish odor, supports combustion of glowing splint
NO	Combines with oxygen of air to form brown nitrogen dioxide
Br <sub>2</sub>	Red liquid, vaporizes easily, irritates throat

## VI. TESTS FOR TEXTILE FIBERS

Test	Animal Fibers		Vegetable Fibers		
	Wool	Silk	Cotton	Linen	Rayon
Heat (flame)	Burns slowly in flame Odor of burnt hair		Continues to burn when removed from flame Odor not unpleasant		
Base (strong) 10% NaOH	Dissolves entirely		Not dissolved		
Acid (conc) HCl	Not affected	Dissolves	Not affected		Dissolves slowly
HNO <sub>3</sub>	Yellow	Yellow	No evident action		No evident action



# VII. PERIODIC TABLE

## THE PERIODIC ARRANGEMENT OF THE ELEMENTS ACCORDING TO ATOMIC NUMBERS

(Atomic Weights Based on Carbon-12)

O INERT GASES															
4 0026	He	2													
20 183	Ne	10													
39 948	Ar	18													
83 80	Kr	36													
131 30	Xe	54													
(222)	Rn	86													
			VIIA												
18 9984	F	9													
15 9994	O	8													
14 0067	N	7													
12 0111	C	6													
10 811	B	5													
28 9815	Al	13													
72 59	Ge	32													
69 72	Ga	31													
53 37	Zn	30													
63 54	Cu	29													
58 71	Ni	28													
58 933	Co	27													
53 647	Fe	26													
54 938	Mn	25													
95 94	Mo	42													
92 906	Nb	41													
91 22	Zr	40													
88 905	Y	39													
87 62	Sr	38													
85 47	Rb	37													
132 905	Cs	55													
137 34	Ba	65													
138 91	La	57													
(227)	Ac	89													
			VIII B												
			II B												
127 60	Te	52													
121 75	Sb	51													
118 69	Sn	50													
114 82	In	49													
107 670	Ag	47													
106 4	Pd	46													
102 905	Rh	45													
101 07	Ru	44													
99	Tc	43													
195 09	Pt	78													
192 2	Ir	77													
190 2	Os	76													
189 948	Ta	73													
186 85	W	74													
183 85	Re	75													
178 49	Hf	72													
176 49	Ti	73													
176 49	Zr	40													
91 22	Y	39													
88 905	La	57													
87 62	Sr	38													
85 47	Rb	37													
132 905	Cs	55													
137 34	Ba	65													
138 91	La	57													
(227)	Ac	89													
			VIIA												
32 064	S	16													
35 453	Cl	17													
39 948	Ar	18													
79 909	Br	35													
78 96	Se	34													
74 922	As	33													
72 59	Ge	32													
69 72	Ga	31													
53 37	Zn	30													
63 54	Cu	29													
58 71	Ni	28													
58 933	Co	27													
53 647	Fe	26													
54 938	Mn	25													
95 94	Mo	42													
92 906	Nb	41													
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85 47	Rb	37													
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53 37	Zn	30													
63 54	Cu	29													
58 71	Ni	28													
58 933	Co	27													
53 647	Fe	26													
54 938	Mn	25													
95 94	Mo	42													
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91 22	Zr	40													
88 905	Y	39													
87 62	Sr	38													
85 47	Rb	37													
132 905	Cs	55													
137 34	Ba	65													
138 91	La	57													
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			VIIA												
32 064	S	16													
35 453	Cl	17													
39 948	Ar	18													
79 909	Br	35													
78 96	Se	34													
74 922	As	33													
72 59	Ge	32													
69 72	Ga	31													
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63 54	Cu	29													
58 71	Ni	28													
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# VIII. THE CHEMICAL COMPOSITION OF SOME FOOD MATERIALS\*

	Water	Protein	Fat	Car- bohy- drate	Ash	Fuel Value per Lb
Apples	84.6	0.4	0.5	14.2	0.3	290
Asparagus, cooked	91.6	2.1	3.3	2.2	0.8	220
Bacon, smoked	20.2	10.5	64.8		5.1	2930
Bananas	75.3	1.3	0.6	22.0	0.8	460
Beans, baked	68.9	6.9	2.5	19.6	2.1	600
Beans, string, canned	93.7	1.1	0.1	3.8	1.3	95
Beefsteak, porterhouse	60.0	21.9	20.4		1.0	1270
Bread, white	35.6	9.3	1.2	52.7	1.2	1205
Butter	11.0	1.0	85.0		3.0	3605
Cabbage	91.6	1.6	0.3	5.6	1.0	145
Candy				96.0		1785
Carrots	88.2	1.1	0.4	9.3	1.0	210
Celery	94.5	1.1	0.1	3.3	1.0	85
Cheese, cottage	72.0	20.9	1.0	4.3	1.8	510
Chicken (fowl)	63.7	19.3	16.3		1.0	1045
Chocolate	5.9	12.9	48.7	30.3	2.2	2860
Consommé	96.0	2.5		0.4	1.1	55
Corn, canned	76.1	2.8	1.2	19.0	0.9	456
Eggs, boiled	73.2	13.2	12.0		0.8	765
Halibut steak	75.4	18.8	5.2		1.0	665
Ham, smoked	39.8	18.5	38.8		4.7	1945
Lettuce	94.7	1.2	0.3	2.9	0.9	90
Macaroni, cooked	78.4	3.0	1.6	15.8	1.3	415
Milk, whole	87.0	3.3	4.0	5.0	0.7	325
Oatmeal gruel	91.6	1.2	0.4	8.3	0.5	155
Oleomargarine	9.5	1.2	83.0		6.3	3525
Olives green	58.0	1.1	27.6	11.6	1.7	1400
Oranges	86.9	0.8	0.2	11.6	0.5	240
Oysters	88.3	6.0	1.3	3.3	1.1	230
Peanuts	9.2	25.8	38.6	24.4	2.0	2560
Peas, canned	85.3	3.6	0.2	9.8	1.1	255
Potatoes, boiled	75.5	2.5	0.1	20.9	1.0	440
Potatoes, sweet, cooked	61.9	3.0	2.1	42.1	0.9	925
Salmon, canned	63.5	21.8	12.1		2.6	915
Sausage, wieners	43.9	28.0	22.1	1.6	4.4	1485
Sauerkraut	88.8	1.7	0.5	3.8	5.2	125
Spinach, cooked	89.8	2.1	4.1	2.6	1.4	260
Strawberries	90.4	1.0	0.6	7.4	0.6	180
Tomatoes, canned	94.0	1.2	0.2	4.0	0.6	105
Walnuts, California	2.5	18.4	64.4	13.0	1.7	3300
Wheat, shredded	8.1	10.5	1.4	77.9	2.1	1700

\* Compiled from Bulletin No 28, U S Department of Agriculture

## IX. TABLE OF PHYSICAL CONSTANTS OF ELEMENTS\*

Element	Symbol	Valence	Atomic Number	Atomic Weight†	Density (g/ml)	Melting Point °C	Boiling Point °C
Actinium	Ac	3	89	(227)		1030 0	
Aluminum	Al	3	13	26 9815	2 70	660 0	2450 0
Americium	Am	3, 4, 5, 6	95	(243)	11 7		
Antimony	Sb	3, 5	51	121 75	6 62	630 5	1380 0
Argon	Ar	0	18	39 949	1 40	-189 4	-185 8
Arsenic	As	±3, 5	33	74 922	5 72	817 0	613 0‡
Astatine	At		85	(210)		(302)	
Barium	Ba	2	56	137.34	3 5	714 0	1640 0
Berkelium	Bk	3, 4	97	(247)			
Beryllium	Be	2	4	9 0122	1 85	1277 0	2770 0
Bismuth	Bi	3, 5	83	208 980	9 8	271 3	1560 0
Boron	B	3	5	10 811	2 34	(2030)	
Bromine	Br	±1, 4, 5	35	79 909	3 12	-7 2	58 0
Cadmium	Cd	2	48	112 40	8 65	320 9	765 0
Calcium	Ca	2	20	40 08	1 55	838 0	1440 0
Californium	Cf	3	98	(251)			
Carbon	C	2, 4	6	12 0111	2 26	3727 0‡	4830 0
Cerium	Ce	3, 4	58	140 12	6 77	804 0	3470 0
Cesium	Cs	1	55	132 905	1 90	28 7	690 0
Chlorine	Cl	±1, 4, 5, 6, 7	17	35 453	1 56	-101 0	-34 7
Chromium	Cr	2, 3, 6	24	51 996	7 19	1875 0	2665 0
Cobalt	Co	2, 3	27	58 933	8 9	1495 0	2900 0
Columbium	SEE Niobium						
Copper	Cu	1, 2	29	63 54	8 96	1083 0	2595 0
Curium	Cm	3	96	(247)			
Dysprosium	Dy	3	66	162 50	8 56	1407 0	2330 0
Einsteinium	Es		99	(254)			
Erbium	Er	3	68	167 26	9 15	1497 0	2630 0
Europium	Eu	2, 3	63	151 96	5 24	828 0	1490 0
Fermium	Fm		100	(253)			
Fluorine	F	-1	9	18 9984	1 11	-219 6	-188 2
Francium	Fr	1	87	(223)		(27)	
Gadolinium	Gd	3	64	157 25	7 87	1312 0	2730 0
Gallium	Ga	2, 3	31	69 72	5 91	29 75	2000±150
Germanium	Ge	4	32	72 59	5 32	937 4	2830 0
Glucium	SEE Beryllium						
Gold	Au	1, 3	79	196 967	19 3	1063 0	2970 0
Hafnium	Hf	4	72	178 49	13 1	2222 0	5400 0
Helium	He	0	2	4 0026	0 126	-269 7	-268 9
Holmium	Ho	3	67	164 930	8 80	1461 0	2330 0
Hydrogen	H	1	1	1 00797	0 071	-259 2	-252 7
Indium	In	3	49	114 82	7 31	156 2	2000 0
Iodine	I	±1, 4, 5, 7	53	126 904	4 94	113 7	183 0
Iridium	Ir	2, 3, 4, 6	77	192 22	22 5	2454 0	5300 0
Iron	Fe	2, 3	26	55 847	7 86	1536 0	3000 0
Krypton	Kr	0	36	83 80	2 6	-157 3	-152 0
Lanthanum	La	3	57	138 91	6 19	920 0	3470 0
Lawrencium	Lw		103				
Lead	Pb	2, 4	82	207 19	11 4	327 4	1725 0
Lithium	Li	1	3	6 939	0 53	108 5	1330 0
Lutecium	Lu	3	71	174 97	9 85	1652 0	1930 0
Magnesium	Mg	2	12	24 312	1 74	650 0	1107 0
Manganese	Mn	2, 3, 4, 6, 7	25	54 938	7 43	1245 0	2150 0

\* The 103 chemical elements known at the present time are included in this table. Some of those recently discovered have been obtained only as unstable isotopes.

† Based on Carbon-12. Figures enclosed in parentheses represent the mass number of the most stable isotope.

‡ Element sublimates unless under pressure.

# IX. TABLE OF PHYSICAL CONSTANTS OF ELEMENTS\*

(Continued)

Element	Symbol	Valence	Atomic Number	Atomic Weight†	Density (g/ml)	Melting Point °C	Boiling Point °C.
Mendelevium	Md		101	(256)			
Mercury	Hg	1 2	80	200.59	13.6	-36.4	357.0
Molybdenum	Mo	2 3 4 5 6	42	95.94	10.2	2610.0	5560.0
Neodymium	Nd	3	60	144.24	7.00	1019.0	3170.0
Neon	Ne	0	10	20.183	1.20	-248.6	-246.0
Neptunium	Np	3 4 5 6	93	(237)	19.5	637.0	
Nickel	Ni	2 3	28	58.71	8.9	1453.0	2730.0
Niobium	Nb	3 5	41	92.906	6.4	2415.0	3300.0
Nitrogen	N	2 ±3 4 5	7	14.0067	0.81	-210.0	-195.8
Nobelium	No		102	(254)			
Osmium	Os	2 3 4 6 8	76	190.2	22.6	2700.0	5500.0
Oxygen	O	-2	8	16.9994	1.14	-218.8	-183.0
Palladium	Pd	2 4	46	106.4	12.0	1552.0	3980.0
Phosphorus	P	±3 4 5	15	30.9738	1.82	44.2	280.0
Platinum	Pt	2 4	78	195.09	21.4	1769.0	4530.0
Plutonium	Pu	3 4 5 6	94	(242)		640.0	3235.0
Polonium	Po	2 4	64	(210)	(9.2)	254.0	
Potassium	K	1	19	39.102	0.86	63.7	760.0
Praseodymium	Pr	3 4	59	140.907	6.77	919.0	3020.0
Promethium	Pm	3	61	(147)		(1077)	
Protactinium	Pa	4 5	91	(231)	15.4	(1230)	
Radium	Ra	2	88	(226)	5.0	700.0	
Radon	Rn	0	86	(222)		(-71)	(-81.8)
Rhenium	Rh	1 2 4 6 7	75	186.2	21.0	3180.0	5900.0
Rhodium	Rh	2 3 4	45	102.905	12.4	1966.0	4500.0
Rubidium	Rb	1	37	85.47	1.53	38.9	688.0
Ruthenium	Ru	2 3 4 6 8	44	101.07	12.2	2500.0	4900.0
Samarium	Sm	2 3	62	150.35	7.49	1072.0	1630.0
Scandium	Sc	3	21	44.956	3.0	1539.0	2730.0
Selenium	Se	-2 4 6	34	78.96	4.79	217.0	685.0
Silicon	Si	4	14	28.086	2.33	1410.0	2650.0
Silver	Ag	1	47	107.870	10.5	960.8	2210.0
Sodium	Na	1	11	22.9898	0.97	97.8	892.0
Strontium	Br	2	38	87.62	2.6	768.0	1380.0
Sulfur	S	-2 3 4 6	16	32.064	2.07	119.0	444.6
Tantalum	Ta	5	73	180.948	16.6	2996.0	5425.0
Technetium	Tc	7	43	(99)	21.5	(2130)	
Tellurium	Te	-2 4 8	52	127.60	6.24	449.5	989.8
Terbium	Tb	3 4	65	158.924	8.25	1356.0	2530.0
Thallium	Tl	1 3	81	204.37	11.85	303.0	1457.0
Thorium	Th	4	90	232.038	11.7	1750.0	3850.0
Thulium	Tm	3	69	168.934	9.32	1545.0	1720.0
Tin	Sn	2 4	50	118.69	7.30	231.9	2270.0
Titanium	Ti	3 4	22	47.90	4.51	1668.0	3260.0
Tungsten	W	2 3 4 5 6	74	183.85	19.3	3410.0	5930.0
Uranium	U	3 4 5 6	92	238.04	19.07	1132.0	3818.0
Vanadium	V	2 3 4 5	23	50.942	6.1	1900.0	3450.0
Xenon	Xe	0	54	131.30	3.06	-111.9	-108.0
Ytterbium	Yb	2 3	70	173.04	8.96	824.0	1530.0
Yttrium	Y	3	39	88.905	4.47	1509.0	3030.0
Zinc	Zn	2	30	65.37	7.14	419.5	906.0
Zirconium	Zr	4	40	91.22	6.49	1852.0	3580.0

\* The 103 chemical elements known at the present time are included in this table. Some of these recently discovered have been obtained only as unstable isotopes.

† Based on Carbon 12. Figures enclosed in parentheses represent the mass number of the most stable isotope.

‡ Element sublimates unless under pressure.

## X. REFERENCE AND COLLATERAL READING

There are many excellent textbooks and periodicals available for reference purposes and for supplementary reading in chemistry and related fields. You will undoubtedly find some of these in your school library. A few representative ones are listed below.

**INORGANIC** Nebergall and Schmidt *General Chemistry*, D. C. Heath and Company. Frey *College Chemistry*, Prentice Hall, Inc. Sisler, Vander Werf, Davidson *College Chemistry*, The Macmillan Company.

**ORGANIC** Wertheim and Jeskey *Introductory Organic Chemistry*, McGraw Hill Book Company. Noller *Textbook of Organic Chemistry*, W. B. Saunders Company. Kelley *Organic Chemistry*, McGraw Hill Book Company. Morrison and Boyd *Organic Chemistry*, Allyn and Bacon.

**PHYSIOLOGICAL** Anderson *Essentials of Physiological Chemistry*, John Wiley and Sons, Inc. Hawk, Oser, Summerson *Practical Physiological Chemistry*, McGraw Hill Book Company. Harrow and Mazur *Textbook of Biochemistry*, W. B. Saunders Company.

**FOOD AND NUTRITION** Sherman *Chemistry of Food and Nutrition*, The Macmillan Company. Mitchell and Bernard *Food in Health and Disease*, F. A. Davis Company. Meyer *Food Chemistry*, Reinhold Publishing Company.

**MISCELLANEOUS** Meyer *Introductory Chemistry*, The Macmillan Company. Weeks *Discovery of the Elements*, Chemical Education Publishing Company, Easton, Pa. Moore *A History of Chemistry*, McGraw Hill Book Company.

**PERIODICALS** In addition to the medical and nursing journals there are numerous periodicals which carry articles of interest to students of chemistry. Such publications as the *Journal of Chemical Education*, the *Scientific American*, the *Chemical and Engineering News*, and *Science* are typical ones. A new periodical, *Chemistry*, by the American Chemical Society, is intended for advanced high school and for college students.

In searching for suitable material for reports, etc., one should not overlook the better *encyclopedias*.

## LABORATORY WORK

### To the Instructor.

At the beginning of each laboratory period the instructor should discuss the experiment with the class, outlining general procedures and clarifying objectives. This eliminates many minor errors, delays, and difficulties that develop if directions are not carefully read and followed.

The experiments are so prepared that the student need answer only one specific question at a time. Each student's work should be individually checked at least once during the laboratory period. The student benefits by such conferences, and the instructor gains a better knowledge of each student's ability. After the mistakes are corrected the instructor initials or rubber stamps the experiment (date accepted). No grade need be given at this time, this can be done at the end of the course. Such a method saves time for the student, makes it easy for the instructor to check the results, and helps him avoid the drudgery of grading notebooks after the laboratory period is over.

Since there are at least two laboratory exercises for most chapters, the first check may be made upon completion of the first exercise, which usually occurs near the middle of the period. Upon completion of all assigned work, before the apparatus is cleaned and put away, the student should bring the work to the instructor for a second and final check up. This method avoids a period end work inspection jam and results in a more orderly and efficient laboratory period. However, at times it may be more convenient to delay this final inspection until the start of the next laboratory period.

Many chemistry instructors in nursing schools are doctors or teachers from high schools and colleges, consequently they do not have the opportunity of becoming acquainted with each individual student. In going over the laboratory work of a student, such an instructor is often embarrassed by inability to remember the student's name. To overcome this difficulty, space has been left at the beginning of each Laboratory Exercise for writing in the student's name, date, and section.

Materials for each exercise usually can be kept in suitable cardboard or wooden boxes, labeled with the number of the exercise and materials lacking, and then shelved. This procedure saves the instructor time in getting material together for each exercise in the next semester course. Also the materials are conveniently ready for any student who is to make up an exercise.

## PART V

# LABORATORY CHEMISTRY

### THE STUDENT'S CHEMICAL WORKSHOP

A Laboratory Investigation To test potency a scientist adds an iodophor to  
polo infected living tissue cultures Courtesy West Chemical Products Inc



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## CHECK LIST OF APPARATUS

Section	Date	Name
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*To the Student*

1 Remove all apparatus from your assigned drawer and cupboard and place on top of your laboratory desk

2 The pieces of *general* apparatus named and illustrated below are for the use of all sections Place them in the cupboard



Tubing and  
burner

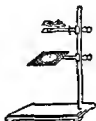


Pneumatic trough

or



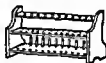
Pan



Ring stand wire  
gauze with asbestos  
center, and burette  
clamp



Mortar and pestle



Test tube rack

3 The following pieces of *individual* apparatus are to be checked, cleaned, and kept in your assigned drawer

*Apparatus*

1 beaker 250 ml  
Pyrex, low  
form



3 bottles wide  
mouth 6 oz  
to take No 5  
stopper



1 evaporating  
dish diameter  
3 inches

*Apparatus*

1 graduate 25 ml



1 litmus  
vial or  
book



1 box safety  
matches



## Apparatus



1 filter paper  
package



1 flask Erlen  
meyer, 250 ml  
Pyrex, to take  
No 5 stopper



1 funnel, diam  
eter  $2\frac{1}{2}$  inches,  
6-inch stem, or  
a funnel tube



3 glass plates  
 $2\frac{1}{4}$ " by  $2\frac{1}{2}$ "



## Apparatus



1 one-hole rubber  
stopper, to fit test  
tube Hole as large  
as in No 5 stopper



1 two hole rubber  
stopper, No 5, to  
fit bottle or flask



12 test tubes 5" by  
 $\frac{5}{8}$ "



1 test tube  
brush



1 test tube  
holder



1 rubber tubing  
8 inches, diam  
eter  $\frac{1}{4}$  inch



4 To protect your clothing, provide yourself with a rubber or plastic apron or other outer garment (smock) unless one is provided Soap and a hand towel or wiping cloth are also desirable

## EXERCISE 1—CHAPTER 1

### PHYSICAL AND CHEMICAL CHANGES

Section      Date      Name

**MATERIALS** Magnesium ribbon silver nitrate solution pieces of cloth potassium iodide mercuric chloride sodium bicarbonate tartaric acid

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#### Instruction

(1) When a question is asked describe in detail what is observed, and where conclusions can be drawn state them briefly in this and all following experiments (2) Expressions preferably printed pertaining to all exercises must be done during the regular laboratory period (3) In carrying out the experiments keep in mind that in every chemical reaction there is a change in composition and in properties of the original substances involved along with an energy change

(a) **TO STUDY THE CHANGE PRODUCED BY BURNING** Examine a piece of magnesium ribbon noticing that it is a lustrous white flexible solid Hold one end with your test tube holder and insert the free end into a flame What happens?

Now examine the product magnesium oxide, and compare it with the properties of the original magnesium How do they differ?

A chemical change as compared to a physical change involves (a) a change in composition of the substance (b) a change in at least some of its original descriptive properties and (c) an energy change Why is the burning of magnesium considered to be a chemical change?

(b) **TO STUDY THE CHANGE PRODUCED BY LIGHT** Place a drop of silver nitrate solution on a piece of white cloth and expose for some time to the light, preferably sunlight The dark appearing spot is amorphous silver What apparent evidence indicates that

light has produced a chemical change?

(c) **TO STUDY THE CHANGE PRODUCED BY HEAT:** Place three or four crystals of potassium iodide and mercuric chloride in a mortar and grind until there is decided evidence of a change. The pink compound formed is mercuric iodide. Why consider that heat (here result of friction) may produce a chemical change?

(d) **TO STUDY THE CHANGE PRODUCED BY WATER:** Into a test tube place a pinch of sodium bicarbonate (baking soda) and an equal amount of tartaric acid crystals. Add some water. Why consider that water is an agent that may bring about a chemical change?

The mixture of baking soda and tartaric acid is very similar in composition to one type of commercial baking powder, and it is also used in making certain effervescing powders.

(e) **SUMMARY:** A chemical change always involves a change in composition and corresponding energy changes. In some cases energy is required and in others energy is given out during chemical change. For example, burning of magnesium produces energy in the form of light and \_\_\_\_\_, while to produce amorphous silver from a solution of silver nitrate, energy in the form of \_\_\_\_\_ is required.

### Instruction:

*Unless otherwise directed, always wash all liquids and soluble solids down the sink with plenty of running water. Waste solids, such as paper toweling, filter paper, and burnt matches should be placed in a waste paper container, while insoluble material, such as broken glass, should be placed in crocks provided for that purpose. Never put paper and glass in the same waste container. Ammonium hydroxide removes silver stains if not too old (p. 673).*

## EXERCISE 2—CHAPTER I

### ELEMENTS, MIXTURES, AND COMPOUNDS

Section      Date      Name

**MATERIALS** *Powdered sulfur (rhombic) powdered iron carbon disulfide, magnet magnifying glass*

(a) Place five grams of sulfur and seven grams of powdered iron on separate sheets of paper. Observe their physical properties, i. e., state, color, magnetic properties, solubility of a pinch in one fourth of a test tube of carbon disulfide. Iron and sulfur are elements. Grind together thoroughly in a mortar the sulfur and iron. Place a pinch of the mixture on a piece of paper and examine with a magnifying glass. Can you distinguish the iron from the sulfur?

Hold a magnet near a small portion of the mixture. Result? What kind of a change?

(b) To a pinch of the mixture in a test tube add about five milliliters (ml) of carbon disulfide (explosive near a flame), shake, and filter into an evaporating dish. To filter, fold a filter paper in half, and then again at right angles to the straight edge. Open the paper



Fig. 1—Making a Filter Cone

as a cone, with a triple layer of paper on one side and a single layer on the other (Fig. 1). Place in a glass funnel. What is the dark substance that remains on the filter paper or in the test tube?

Allow the liquid (filtrate) in the evaporating dish to evaporate (do not heat).

What is in the solid residue?

What kind of a change has taken place?

(c) Place the remaining portion of the mixture in a test tube, clamp, and heat the lower part of the tube (Fig. 2), cautiously at first, then strongly to a red heat (10 min ) while noticing the different changes. What evidence is there that chemical action took place in the mixture?

Incline test tube loosely clamped near mouth

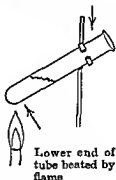


Fig. 2—A Mixture Under Heat

Allow the test tube to cool, and then break it in the mortar. Compare the physical properties of the substance left with the original mixture. Can you now distinguish between the iron and sulfur by means of a magnifying glass?

Has the magnet any effect upon the substance?

Of what is the substance composed?

When elements combine chemically, do they retain their original properties?

What is the new substance formed by the combining of two or more elements?

Besides a change in *composition* and physical properties, what other characteristic do all chemical changes have?

How does a compound differ from a mixture?

(d) SUMMARY: Complete the following statements

An element is

A compound is

A mixture is

## EXERCISE 3—CHAPTER II

### GLASS WORKING

Section . Date . Name .

**MATERIALS** *Two feet of glass tubing, triangular file; wing top.*

**To the Instructor:** *The technique required in the manipulation of glass tubing should first be demonstrated before the class, provided students have had no previous experience in glass working*

(a) **TO CUT GLASS TUBING:** Obtain from the supply table, or room, the materials listed above; lay the tube on the laboratory table, and with the file make a deep transverse scratch in the middle of the tube. Grasp the tube as shown in Fig. 3, holding the thumbs,



Fig. 3—Break Glass by Shoving with the Thumbs Back of Scratched Place.

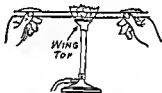


Fig. 4—Softening Glass Tubing by Heat Prior to Bending.

one on each side of the scratch, opposite to the side of the scratch, and push gently with the thumbs. For large glass tubing it may be necessary to make a deeper scratch completely around the tubing or rod

(b) **TO BEND GLASS TUBING:** Place the wing top on the burner, light the gas, and adjust the air holes at the bottom of the burner in order to secure a nonluminous flame. Hold the tube, as shown in Fig. 4 lengthwise, in the upper part of the broad flame, rotating it slowly so that the heat will be uniformly distributed on all sides. Continue the heating and rotating until the glass becomes soft enough to bend under its own weight. Remove from the flame and bend slowly to a right angle (Fig. 5). If the tube does not bend easily rebait and try again. Support the bot bend across some object so that the glass may cool slowly and not burn the desk. Later during the laboratory period when the glass is cool, make one arm of the right angle bend about two inches long, and the other end about five inches long.

Fire-polish the ends as directed in (c).



(c) **TO FIRE-POLISH OR SEAL THE END OF GLASS TUBING:** Remove the wing top from the burner, and using the remaining half (one foot) of the original glass tubing (or a glass rod if provided), hold the end of the glass, as shown in Fig. 6, in the blue or *non-luminous* upper edge of the flame. This is a hotter flame than the yellow flame. Rotate the tube while heating, until you can see that the sharp edges of the glass are becoming soft and yellow in color. If the glass tubing is to be sealed at one end, or a glass rod is to be rounded, the tube or rod will need to be held for a longer time in

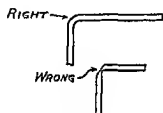


Fig. 5—Round and Flat Bends.



Fig. 6—Smoothing the End of a Glass Rod or Tube.

the upper and hottest part of this flame. Support the hot end so that it will cool slowly and not burn the desk.

If your right-angle bend is cool, cut to the dimensions as indicated in (b) and then fire-polish. Cut the sealed tube or rounded rod in the middle and preserve as a stirring rod.

(d) **TO DRAW OUT GLASS TUBING:** Using the remaining six-inch piece of glass tubing, heat lengthwise in the nonluminous flame until *very soft*. Remove it from the flame and immediately pull until drawn out, as shown in Fig. 7, to a little over half again its original



Fig. 7—Drawn Apart.

length. Cool and cut in the center. Save one as a dropping tube or pipette. Submit the right-angle tube and the stirring rod to the

Instructor for inspection and credit .

**Instruction:** Remember that broken glass is to be placed in a separate waste container.

## EXERCISE 4—CHAPTER II

## MEASUREMENT OF LABORATORY VESSELS

Section      Date      Name

**MATERIALS** *Graduated cylinder, various vessels in laboratory drawer, balance*

**NOTE** The metric system of measurement is used in all scientific measurements. The unit of length is the *meter* (39.37 inches) which is divided into 100 centimeters (Fig. 8).

The unit of volume is the *liter* (1.05 quarts), which is composed of 1000 milliliters (ml) frequently called cubic centimeters (cc). The unit of weight is the *kilogram* which is the weight of 1000 milliliters of water at 4° C (Fig. 9). Each milliliter of water weighs one gram.

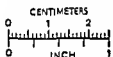
Remember

1 meter (m) = 100 centimeters (cm) = 1000 millimeters (mm)

1 liter (l) = 1000 milliliters (ml) or cubic centimeters (cc)

1 kilogram (kg) = 1000 grams (Gm) = 2.2 pounds

#### STANDARDS OF LINEAL MEASUREMENT



2.54 centimeters equals one inch

#### SPACE STANDARD COMPARED WITH WEIGHT STANDARD



1 ml. of water weighs 1 Gm

Fig. 8—What Are the Advantages of These Two Standards?

Fig. 9—How Is This Used in Chemistry of Health and Disease?

(a) **A MENTAL CONCEPT OF VARIOUS VOLUMES** Add water to the graduated cylinder until the lower part of the curved surface, called the *meniscus*, reads 5 ml. Pour this water into one of your test tubes and mark the upper level of the water. Add 5 ml more of water and mark the upper level, and remember the approximate amount to be used when an experiment calls for 5 or 10 ml of a liquid. Add sufficient water to fill the test tube, and measure the amount by use of the graduate. Record it.

Remember this volume held by the test tube, so that you can make approximate measurements in the future. It is also convenient to know how much of the lower curved portion of the test tube is required to hold 1 ml. Try it.

(b) **APPROXIMATE VOLUMES OF OTHER LABORATORY VESSELS** Pour 25 ml, 50 ml, and 100 ml portions of water into your beaker.

flask, and evaporating dish until you know the approximate amount of liquid contained in these vessels, or parts of them.

Test tube holds	ml
Beaker holds	ml.
Flask holds	ml
Evaporating dish holds	ml.
Bottle holds	ml.

In all following exercises estimate instead of measuring metric volumes, unless unusual accuracy is required.

(c) **MEASUREMENT OF WEIGHTS.** The trip scale, triple beam balance with a capacity of 610 Gm. and a sensitiveness of 0.1 Gm makes a very satisfactory balance for general laboratory purposes. Time is saved in weighing and no weights are ever lost or misplaced. Place a beaker on the left pan of the balance and weigh (Fig. 10). Pour 100 ml of water into the beaker and weigh again. Record the weights below. If density is the weight divided by the volume, what is the density of water in grams per milliliter?

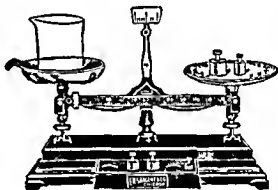


Fig 10—Laboratory Balance for Weighing

Record your figures in the following table:

Wt of beaker + water	Gm
Wt. of beaker	Gm
Wt of 100 ml of water	Gm
Density of water in grams per ml	Gm

Considering that hydrochloric acid has a density of 1.2 grams per ml., what would be the weight of 100 ml. of hydrochloric acid?

(d) **SUMMARY:** In scientific measurement the system is used. Its chief advantage lies in its ease of making calculations, since the relationship between the units is on a basis of ten.

## EXERCISE 5—CHAPTER II

### LIMEWATER

Section      Date      Name

Limewater is a saturated solution of calcium hydroxide. It should contain not less than 0.14 per cent of  $\text{Ca}(\text{OH})_2$  at  $25^\circ \text{C}$ . Preserve it in well-filled tightly stoppered bottles.

**MATERIAL:** *Lime*

Fill the curved bottom of a test tube with powdered lime. Fill the test tube almost completely with distilled water and shake vigorously for several minutes in order to form a saturated solution of the white solid, namely, calcium hydroxide. Filter (Fig. 11) and use the clear limewater for the rest of the experiment.

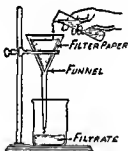


Fig 11—Filtering

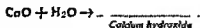


Fig 12—Heating

(a) Using freshly prepared limewater, record the taste

What is its action on red litmus paper?

(b) Complete the equation for the reaction which takes place when water is added to quicklime by making the formula for calcium hydroxide.

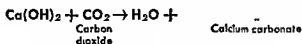


What is a common name for the white solid formed?

Is it very soluble?

(c) Pour several drops of limewater on a glass plate and allow to stand exposed to the air for a few minutes. By means of a glass

tube blow air through some limewater contained in a test tube. Observe the formation of a white insoluble precipitate \* Complete the equation for the reaction by making the formula for calcium carbonate



What is the name of the solid formed?

What is the scum formed on the surface of the limewater on the glass plate?

Why should limewater be preserved in well-filled, tightly stoppered bottles?

(d) INSTRUCTION: *When heating a liquid in a test tube (Fig. 12) always hold the tube in an inclined position with the mouth of the tube away from anybody, and slightly agitate the liquid by a sidewise shaking of the tube. Never heat the tube above the surface of the enclosed liquid.*

Heat some clear limewater in a test tube. Examine carefully in a good light. Does the solubility of the calcium hydroxide in the water increase or decrease with rise in temperature?

(e) SUMMARY: A filtrate is defined as

A saturated solution is

The test for carbon dioxide is

Do all solids increase in solubility with rise in temperature?

Any remaining time may be devoted to practice in formula and equation writing.

\* A precipitate is an insoluble substance formed in a liquid. In some cases the precipitate does not settle out, but remains suspended and imparts a cloudiness to the liquid.

## EXERCISE 6—CHAPTER III

## OXYGEN: PREPARATION AND PROPERTIES

Section      Date      Name

**MATERIALS** Potassium chlorate, pulverized manganese dioxide, charcoal, sulfur, sodium, steel wool Deflagrating spoon (most satisfactorily made from 8 inch piece of heavy soft iron wire, flattened at the end and bend at right angle)

**Preparation:**

Add to about one-third of a test tube of potassium chlorate, one-tenth as much pulverized manganese dioxide (catalytic agent). Place your thumb over the mouth of the test tube and mix contents of the tube by shaking it. Push (by a rotary motion) the moistened end of a right-angled glass tube, into a single-hole rubber stopper which fits this test tube. Moisten the end of a piece of narrow rubber tubing eight inches long, and slip it over the other end of the right-angle tube. Place the stopper in the test tube and clamp the tube in a horizontal position. Tap the test tube gently in order to distribute the mixture along the lower side (Fig. 13).

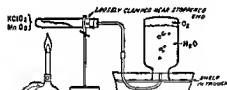


Fig 13—To Note the Physical Properties of Oxygen

Partly fill the pneumatic trough with water and invert in it three bottles filled with water. Heat the test tube gently, so that there will be a slow evolution of oxygen. Now collect three bottles full of gas, covering each when filled with a glass plate and set them mouth upwards on the table. The slight cloud that is often present when oxygen is prepared from potassium chlorate and manganese dioxide is due to an impurity and shortly disappears if the gas is left to stand over water.

Complete the following equation:

Potassium chlorate  $\rightarrow$  Potassium chloride + Oxygen



## A. PHYSICAL PROPERTIES

From observations and study state the physical properties of oxygen, namely: Physical state , color , taste and solubility in water .

## B. CHEMICAL PROPERTIES

(a) CARBON: Lower a piece of glowing charcoal contained in a deflagrating spoon into one bottle of oxygen (Fig. 14) and keep there until all action is over. Remove the spoon and cover the top of the bottle with a glass plate. Result?

Of what is the resulting gas composed?

The chemical name for the product formed is

Write the equation:

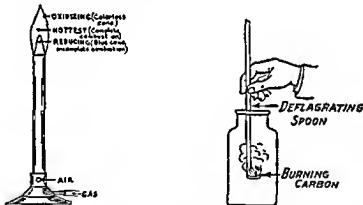


Fig. 14—Does Carbon Have an Affinity for Oxygen?

Remove the glass plate and add one-half a test tube of water. Close with the hand and shake thoroughly for at least a minute in order to dissolve all of the gas in the water. Place a strip of blue litmus paper in the bottle. Result?

Litmus paper turns red in the presence of an acid, and all acids contain hydrogen. Litmus paper turns blue in the presence of a base, and all bases contain oxygen bound to hydrogen in what is known as a hydroxyl group (OH). Verify by looking at the formulas on the bottles of acids and bases.

Does the oxide of carbon dissolved in water form an acid or a base?

Pour the solution into a clean test tube, and to this solution add a few milliliters of limewater. If there is no apparent change, look down through the liquid in the test tube in the presence of good light. Result?

Calcium hydroxide (limewater) is a test for carbon dioxide and for carbonic acid (p 649).

(b) **SULFUR:** Put a pinch of sulfur in the deflagrating spoon and hold in the upper part of the laboratory flame until the sulfur begins to burn (kindling temperature). Observe the color and the size of the flame. Now lower the burning sulfur into a bottle of oxygen.

Result as to change?

Remove the spoon, cautiously smell the gas in the bottle by fanning some of the gas toward you with your hand. Describe the odor.

Of what is the gas composed?

Write a possible name for this gas

Considering the valence of sulfur to be four, write the equation



Place both red and blue litmus paper in the bottle, add one half a test tube of water, close with the hand and shake. What does the change in color of the litmus paper indicate?

(c) **SODIUM:** (Demonstration by Instructor.) Clean the spoon and place a small piece of metallic sodium on it. Hold at arm's length, warm until the sodium begins to burn and then immediately thrust it into a bottle of oxygen. Result?



Of what is the product composed?

Is it a solid or a gas?

Write a possible chemical name

for the product formed

Write the equation

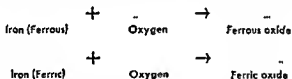


Place both red and blue litmus paper in the bottle, add a little water, remove the spoon, close the mouth of the bottle with your hand and shake it. Result?

What does the color indicate?

(d) IRON: Twist a piece of steel wool around the spoon end of the deflagrating spoon. Ignite it and immediately lower it into a bottle of oxygen. Result?

Observe the solid combustion product. The compound formed, magnetic oxide,  $\text{Fe}_3\text{O}_4$ , is a combination of ferrous oxide and ferric oxide. Write the equations for the formation of each oxide.

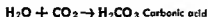


(e) What is formed when elements burn in oxygen or air?

Make a general statement as to the relative intensity of burning in oxygen and in air.

When oxides of elements combine with water and give acid reactions to litmus paper those elements are classified as *nonmetals*. When oxides of elements give a basic reaction (turn red litmus blue) in water, these elements are classified as *metals*. How would you classify sulfur, carbon and sodium? Any oxide of an element which

combines with water to form either an acid or a base (hydroxide) is called an *anhydride*. The nonmetallic oxides that form acids are called *acid anhydrides*. Likewise the metallic oxides forming bases are called *basic anhydrides*. Anhydride means "without water." In the following equations:



the *acid anhydride* is

while

is a *basic anhydride*.

### Summary:

In the preparation of oxygen from potassium chlorate, why is manganese dioxide called a catalytic agent?

Is oxygen active at ordinary temperatures?

An oxidizing agent, as potassium chlorate, is one that

Kindling temperature is defined as

The products of oxidation are called

Anhydrides are \_\_\_\_\_ of metals or nonmetals

An element whose oxide reacts with water to form a base is classified as a

If an acid is produced the element is classified as a

### Instruction:

*Disconnect glass tubing in this and all following experiments from rubber stoppers and tubing before leaving the laboratory.*

## EXERCISE 7—CHAPTER IV

### WATER: DISTILLATION OF WATER

Section      Date      Name

**MATERIALS** *Potassium permanganate crystals, salt, phenolphthalein solution, bent glass condensing tube*

(a) Set up the apparatus as shown in Fig. 15. Pour into the flask 100 ml. of water and add two or three crystals of potassium permanganate and a big pinch of salt. Heat the contents of the flask to boiling and collect a few milliliters of the condensed steam (distillate). If there is no distilled water in the laboratory you will need to collect approximately two test tubes for the next experiment. Is the process of distillation

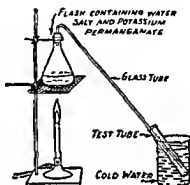


Fig. 15—Distillation of Water.

physical or chemical?

Taste the distillate. What two evidences are there that the water has been purified by distillation?

What substances in the original liquid do not vaporize under the conditions of the experiment?

How could salt water be

converted into fresh water?

Record the taste of the distilled water

How do you account for the taste of boiled or distilled water

Suggest a method for improv-

ing its taste

(b) Add a drop of phenolphthalein to some distilled water in a test tube. (Phenolphthalein is an indicator which turns red in the presence of a trace of a strong alkali.) Result?

To a test tube of tap water add one drop of concentrated ammonia water\* (ammonium hydroxide,  $\text{NH}_4\text{OH}$ ) and a drop of phenolphthalein. Result?

Phenolphthalein is used as a test for any hydroxide solution.

(c) Almost fill one of your six-ounce bottles with tap water, and by means of a clean, dry dropping tube or glass rod, remove and add one drop of concentrated ammonia water. Pour into a clean flask and distill. Collect one-half a test tube of the distillate in each of six clean test tubes; each test tube containing one drop of phenolphthalein. When the water in the beaker becomes hot, change it for cold water. (If Exercise 8 is to be performed, proceed with it while collecting the six tubes of distillate.) Save and check the

six tubes with the Instructor

What evidence

is there that the ammonia passes over with the steam?

Do the first portions of the distillate contain more or less ammonia than the latter portions?

In what manner does ammonia, as an impurity, differ from the salt and potassium permanganate of part (a)?

From what type of impurities can water be freed by distillation?

(d) Place four or five drops of the distilled water in a clean evaporating dish and evaporate, holding the evaporating dish a few inches above the tip of the flame. Is there any residue?

Repeat, using city water.

Why is distilled water used for so many laboratory experiments in preference to city water?

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\* See Fig 17, page 687, for technique of removing stopper, pouring, and measuring, if not previously taught

## EXERCISE 8—CHAPTER IV

### SOFTENING HARD WATERS

Section      Date      Name

**MATERIALS** *Saturated calcium sulfate solution, magnesium sulfate solution (1 2500), borax, sodium carbonate, sodium phosphate, clear soap solution, distilled water* Read *Soap*, pages 361-365

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(a) To a test tube half full of distilled water add a drop of soap solution. Close the mouth of the test tube with your thumb and shake the tube thoroughly. Allow the tube to stand undisturbed for about two minutes. Are the suds permanent?

Has a precipitate formed in the solution?

(b) Using one-half a test tube of faucet water instead of distilled water, repeat (a). If permanent suds do not form with one drop of soap solution, continue adding soap solution and shaking until the suds formed are permanent. Has a precipitate formed?

(c) Using one-half a test tube of distilled water which has been made hard by the addition of a few drops of calcium sulfate solution, repeat experiment (b). How do your results compare with those in (b)?

When suds form, has hard water been made soft?

Can soap be used to soften hard water?

(d) Using one-half a test tube of distilled water which has been made hard by the addition of a few drops of magnesium sulfate solution, repeat experiment (b). Are the results similar to those of (c)?

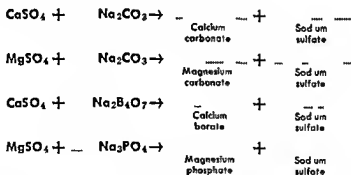
(e) Using one-half a test tube of distilled water which has been made hard by the addition of a few drops of either magnesium sulfate or calcium sulfate solution, add a sufficient number of drops of soap solution to produce a precipitate, but not enough to form suds upon shaking. Rub a small amount of the precipitate between your fingers. Results?

State your reasons why hard water is unsuitable for laundry use

(f) Evaporate a few milliliters of water rendered hard by either calcium or magnesium salt solutions. State your reasons why hard water is unsuitable for steam boilers

(g) Dissolve a pinch of sodium carbonate (washing soda) in one half a test tube of hard water, add a drop of soap solution and shake the tube thoroughly. Continue adding soap solution and shaking until suds form. Keep in mind the number of drops of soap used. Instead of washing soda, use borax and repeat again. Repeat again, but this time use sodium phosphate. Conclusion

Complete the following indicated equations



**Summary:** Hard water contains, primarily, compounds of the metals \_\_\_\_\_ and \_\_\_\_\_

Hard water may be softened by the addition of \_\_\_\_\_

## EXERCISE 9—CHAPTER V

### SOLUTIONS

Section	Date	Name
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**MATERIALS:** Potassium nitrate, "hypo," copper sulfate crystals, sheet gelatin, animal charcoal (bone black), dilute litmus solution, sodium chloride solution, silver nitrate solution. (The carrot demonstration, Exercise 10 B (c) should be started at the beginning of the laboratory period by the Instructor.)

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#### A. THE EFFECT OF TEMPERATURE UPON SOLUBILITY

(a) Measure out two-thirds of a test tube of powdered potassium nitrate. Add this, a little at a time with constant shaking, to a test tube containing 5 ml. of water. When no more will dissolve, pour this solution into another test tube. Feel the lower part of the test tube. Result?

Heat slowly this saturated solution of potassium nitrate until it begins to steam, adding potassium nitrate in small amounts with constant shaking or agitation, until no more salt dissolves. Allow this test tube solution to cool to the temperature of the room. Does it require much more potassium nitrate at a high temperature than it does at a lower temperature for saturation?

Compare and record the effect of temperature on the solubility

(b) Recall or repeat the experiment (p. 649) on the effect of beating one-half a test tube of limewater. Does an increase in temperature always increase the solubility of a solid?

#### B. SUPERSATURATED SOLUTIONS

(a) Fill a test tube one-half full of sodium thiosulfate crystals ("hypo"). If the "hypo" crystals are covered with a white powder due to the loss of water, a few drops of water must be added. Sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ , is chosen since it already contains sufficient water to make a solution at higher temperature. Heat cautiously with a small flame until a clear solution results. If necessary, raise to the boiling point. Place the test tube in a beaker

or bottle of water and allow to cool undisturbed. If a solid should settle out, redissolve by heat and repeat the experiment. The solution is now supersaturated. Drop a tiny crystal of "hypo" into the cold liquid. Result?

Feel the lower part of test tube. Result?

Substances which crystallize out of solution always show this change of temperature, *e. g.*, water to ice. The heat absorbed when the "hypo" dissolves equals the heat given off when it crystallizes. Crystalline substances when added to water as in (a) upon being dissolved always absorb heat. Advantage of this fact is taken in preparing freezing mixtures. In fact whenever a substance changes its state, heat is either liberated or absorbed. This principle is applied in refrigeration.

### C. FACTORS IN MAKING A QUICK SOLUTION

A mass dissolves at its surface only. The larger the total surface, the faster it dissolves. Therefore, when a solution is to be prepared quickly, the solid should be powdered.

(a) Take two crystals of copper sulfate of equal size, which will slip into a test tube. Place one crystal in a test tube and, after pulverizing the second crystal in a mortar, place the powdered copper sulfate in a second test tube. Fill each test tube two-thirds full of water. Place your thumb over the mouth of each tube and shake it gently, noting the time for the powder to go into solution. What fraction of the original crystal remains in the first tube?

To save time, in what form should you use a solid to be quickly dissolved? Save for 10B (a) the tube containing the dissolved powdered copper sulfate.

(b) Warm the test tube containing the undissolved copper sulfate. What effect has heat upon solution? (The color of the solution will indicate the amount of copper sulfate that has dissolved.)



(c) Would stirring aid in dissolving a solid?

Why?

In the process of digestion foods are changed into soluble substances. Why, then, should food be well chewed?

Solution of a solid in a liquid is hastened by several factors, namely , , and

#### D SOME PROPERTIES OF COLLOIDS

(a) **ADSORPTION** Heat about one gram of animal charcoal (bone black) in a porcelain dish for a few minutes. This is to activate the charcoal by expelling the occluded gases. When the charcoal has cooled place enough of it in a test tube to fill the rounded portion of the tube. Add enough dilute litmus solution to half fill the tube and shake the tube and its contents vigorously for at least one minute. Filter out the charcoal through two thicknesses of folded filter paper (or one sheet of quantitative paper) and compare the filtrate with some of the original litmus solution. Result?

The condensing of gases or dissolved substances on the surface of colloids is called

(b) **IMBIBITION** Cut sheet gelatin into two equal sized pieces, about  $\frac{1}{4}$  by  $\frac{1}{4}$  inch. Place one piece in a test tube and cover with cold water. After several minutes compare its size with the remaining dry piece of gelatin. Result?

The swelling of a colloid in a water solution is called

Save the gelatin-water solution for (c).

(c) **PROTECTING ACTION OF A COLLOID:** To keep dispersed material from running together and forming larger particles which settle out a protective colloid may be used.

To one-half a test tube of sodium chloride solution add five drops of silver nitrate solution and stir thoroughly with a glass rod. Place in the test tube rack.

To another test tube one-half full of sodium chloride solution add about 1 ml. of gelatin solution saved from (b), mix thoroughly, and then add five drops of silver nitrate solution. Stir thoroughly with a glass rod and stand in the test tube rack along side of the other tube. Observe from time to time as you proceed with your other experiments.

In the one tube a precipitate of  $\text{AgCl}$  formed and settled. In the test tube containing the gelatin, the  $\text{AgCl}$  remained suspended in what is called a state.

How do you imagine gelatin acts as a protective colloid?

## EXERCISE 10—CHAPTER V

### DIFFUSION, OSMOSIS, DIALYSIS

Section	Date	Name	.
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**MATERIALS** Copper sulfate solution, 0.85 per cent sodium chloride solution, saturated potassium ferrocyanide solution, carrot, saturated sugar solution or molasses, bit, blood lancet or needle, starch, iodine solution, copper sulfate, collodion (or cellophane sausage skins obtained from Visking Corporation, Union Stock Yards, Chicago, or vegetable parchment in 6" x 6" sheets, "Patapar," in box of 1000 sheets), thread

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**To the Instructor:** To save time part B lends itself to demonstration.

#### A. DIFFUSION

Tie a thread to a crystal of copper sulfate and suspend it in a test tube of water. Hold the tube before your eyes in a strong light and observe what is happening.

What name is given to this phenomenon?

What causes the dissolved particles to move?

Where is the pressure greater?

Where is the concentration greater?

#### B. OSMOSIS

(a) Fill a test tube with a copper sulfate solution (decided blue) and introduce into this solution a drop of concentrated solution of potassium ferrocyanide by letting it drop from a glass dropping

tube, the end of which is just above (1 cm.) the surface of the copper sulfate. (If the drop falls to the bottom and breaks, repeat the experiment, using a stronger solution of copper sulfate.) Red copper ferrocyanide is precipitated, forming a semipermeable membrane, which surrounds the drop.

In a few minutes observe the drop. What has happened to the size of the drop?

Explain what produces this result.

(b) Dissolve a drop of blood\* into a test tube full of distilled water, and another drop into a test tube full of physiological saline solution.

How do you account for the fact that in one test tube there is a turbid suspension of blood cells, while in the other, only a clear, pinkish red solution?

The result obtained in (a) and (b) is analogous to that of introducing into the body a hypotonic saline solution after a hemorrhage. This is an illustration of what?

If a drop of dilute copper sulfate were added to a concentrated solution of potassium ferrocyanide, the drop would shrink. This is an illustration of what?

(c) (Demonstration by Instructor): Use a hot or cork borer and make a hole about halfway through a carrot, beginning from the top.† Then fill the hole with molasses or saturated sugar solution.

\* Use a sterilized blood lancet or needle to obtain blood from the ear lobe or finger.

† If the carrot is old, it may be necessary to scrape off lightly the outside epidermis with a knife.

Fit the hole tightly\* with a one-hole stopper, holding a glass tube about one yard long, and immerse the lower half of the carrot in a beaker of water (Fig. 16). Label the level of the sugar solution in the glass tube, and allow to stand an hour or until the next day. Why does the solution rise in the tube?

Besides in the blood, where does osmosis occur in the body?

The passage or diffusion of solvent molecules is called

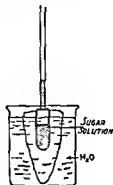


Fig. 16—Osmosis  
in a Carrot.

### C. DIALYSIS

(a) **DIALYZING TUBE:** Prepare a collodion bag by filling to the top a dry, clean test tube with collodion. Pour the collodion immediately into the original container, invert the test tube and clamp it to a ring stand. While the collodion bag is drying proceed to (b). After about five minutes, when no odor of ether is noticeable, fill with tepid water, loosen the edges of the film at the rim of the test tube with your fingernail or some sharp instrument such as a knife, and then with a pencil between the membrane and the test tube carefully loosen the membrane to the bottom of the tube. Proceed to (c).

(b) **COLLOID AND CRYSTALLOID SOLUTIONS:** Prepare a colloidal starch solution by bringing to the boiling point less than a pinch of starch (the amount that would stick to one finger) in half a test tube of water. Prepare a crystalloid solution by dissolving (do not heat) sufficient copper sulfate in half a test tube of water to impart to it a clear deep blue color. Hold both test tubes in a ray of light. How does the colloidal solution look?

\* Melted paraffin or candle grease dropped around the inserted stopper will assure a tight fit.

Filter the starch solution and when cool test a few milliliters of the filtrate with one drop of dilute iodine solution. A blue color indicates the presence of starch. Can a colloid be separated by filter paper?

Mix the two solutions of copper sulfate and iodine free starch, and save for (c). Finish (a).

(c) DIALYSIS: Using a pencil or tube, carefully loosen and remove the collodion membrane from the test tube, pour out the water, partially fill it with the mixture of copper sulfate and starch. Wash off any solution spilled on the outside of the bag, lower the bag into a 25 ml. graduate or beaker half full of water (preferably distilled), allowing the top of the membrane to hang over the rim of the glass. At the end of five minutes or more remove the bag and look down through the liquid in the graduate. The blue color

indicates the presence of iodine to the water in the graduate or beaker. Is there any starch in the distilled water? Add a drop of iodine to the water in the graduate or beaker. What type of solutions

are retained by a membrane?

Are colloidal particles larger or smaller than the molecules of crystalloids?

Would you think that colloidal foods, such as starch, proteins, and emulsions, would be directly absorbable from the alimentary canal?

Before colloidal foods may be absorbed through the intestinal wall into the blood stream they must be disintegrated into a more finely dispersed state by the chemical process called

In a post-mortem examination following the suspicion of poisoning with a metallic salt, such as that of lead, arsenic, or copper, the separation of the crystalloid from the colloidal material of the body (food, albumin, etc.) is done by a process called

Define dialysis

## EXERCISE 11—CHAPTER VI

### IONIZATION

Section      Date      Name

**MATERIALS** *Glacial acetic acid, conc sulfuric acid, zinc, calcium hydroxide, sodium chloride, silver nitrate, sugar, ethyl alcohol, chloroform, and silver nitrate solution*

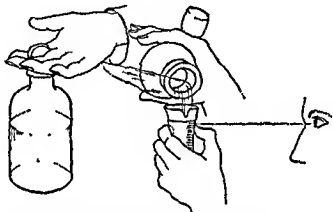


Fig 17

**Instruction:** Study drawing for technic of removing stopper, pouring, and measuring. In case acids, bases, or other chemicals are spilled or spattered on clothing or skin, or in the eyes, wash immediately with large quantities of water (preferably running water). Have someone notify the instructor.

#### A. ELECTROLYTES

1. **ACIDS** (a) Into a dry test tube pour about 2 ml of glacial acetic acid obtained from the supply table. Dip a dry glass rod into the acid, transfer a drop of it to an evaporating dish, and then lay a strip or piece of dry blue litmus paper on the top of the drop of acid

Is there any immediate action noticeable?

Add a drop of water to the acid and the blue litmus paper. The color of the litmus is now

What is necessary

for the acid to react with the blue litmus?

(b) Drop a small, dry piece of zinc into 2 ml of concentrated sulfuric acid contained in a test tube. Is there much evidence that a gas is being evolved?

Into a second test tube half full of water, slowly pour the acid and then add the zinc. Besides the heat generated what apparent evidence is there that chemical action is taking place?

What is necessary for the acid to react with the metal zinc?

Does the dilute  $H_2SO_4$  show any properties that concentrated  $H_2SO_4$  does not show? Will zinc readily displace  $H_2$  from concentrated sulfuric acid that is not diluted or ionized?

The reactions in (a) and (b) are the result of ionization,\* and to cause ionization must be present. Write the equation for the ionization of sulfuric acid, that is, show how the acid molecule breaks up in water, one part becoming positively charged and the other negatively charged.



What ion is responsible for the characteristic action of acids?

2 BASES Place a piece of dry red litmus paper upon a pinch of dry calcium hydroxide. Result? Add a few

drops of water. The color of the litmus is now. Does water bring out any properties which the dry material does not indicate? Do dry hydroxides give the test for hydroxyl ions? Red litmus paper

turns in the presence of hydroxyl ions. Write the equation for the ionization of calcium hydroxide showing the formation of positive and negative fragments.



\* Refer to text for explanation of ionization



What ion is responsible for the characteristic action of bases?

3. **SALTS.** Dissolve one crystal of sodium chloride and one very small crystal of silver nitrate in separate *clean* test tubes containing a few ml of distilled water. Mix the two clear solutions. Result?

Silver nitrate solution is used as a test for the chloride ion. If an electrolyte (acid, base, salt) is insoluble, will it show ionization?

Remembering that the salt, silver chloride, is *insoluble*, complete the following ionic equation



### B. NONELECTROLYTES

Rinse three clean test tubes with distilled water. In one test tube containing distilled water dissolve a few crystals of sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ), and in another test tube containing distilled water dissolve a few milliliters of alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ). Mix in the third test tube a few milliliters of chloroform ( $\text{CHCl}_3$ ) and distilled water. Make a test for the hydrogen ion with blue litmus paper, the hydroxyl ion with red litmus paper, and the chloride ion with silver nitrate solution. Do you get positive tests for these ions?

**Summary:** What classes of substances ionize?

In general if a rapid reaction takes place in solution, is it probably between ions or molecules?

Which are more active chemically in solution, electrolytes or nonelectrolytes?

Why do nonelectrolytes not ionize?

What type of valence exists in nonelectrolytes and compound radicals?

## EXERCISE 12—CHAPTER VI

### STAINS

Section	Date	Name	..	...	....	. . .
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**MATERIALS** *Bleaching powder, sodium carbonate, saturated oxalic acid solution, hydrogen peroxide, potassium permanganate, citric acid solution, Carbona, alcohol, turpentine, borax, "hypo," ammonium hydroxide, starch Pieces of muslin discolored by various stains, as ink, paint, mildew, etc.*

Stains of a physical nature, such as a grease spot, are easily removed by finding the right solvent; but if the stain has been formed by a chemical action, as an ink spot, then a chemical reaction is necessary to change it over into a soluble form so that it may be washed out.

Home and Garden Bulletin no. 62 of the U. S. Department of Agriculture, on the removal of stains, may be obtained at nominal cost by writing directly to that Department. If this bulletin is available, remove all stains from the pieces of cloth given you by the Instructor according to the methods in this bulletin, or in the accompanying directions

#### Chlorine Bleach:

Place 10 Gm. of bleaching powder (chlorinated lime) in a 250 ml. beaker. Add a solution of 10 Gm. of washing soda dissolved in 100 ml. of water. Stir thoroughly, allow the mixture to settle, and filter the supernatant liquid. This clear solution is a good bleach, but must not be left too long on the clothes. When treating stains with this solution, stretch the stained portion over an evaporating dish, or a beaker, and apply the bleach with a medicine dropper or glass tube. Neutralize the chlorine bleach with oxalic acid solution and rinse well in water. Repeat many times if necessary. Ink eradicators are composed of such solutions. Chlorine bleaches must not be used on animal fiber.

#### Potassium Permanganate:

Dissolve several crystals of potassium permanganate in less than a milliliter of water so as to make a concentrated solution. Apply to the stain with a glass rod or tube, and allow it to remain for five minutes on the stain. The brown stain is removed by applying hydrogen peroxide made slightly acid by a drop of hydrochloric acid. Repeat if necessary. Rinse well.

Obtain from the Instructor pieces of stained goods. Remove the stains and return the goods for record.



Fig 18—Stain Removal Treating a stain on nonwashable article with sodium perborate bleach Apply a solution of sodium perborate Rinse well using a small syringe to force water through the spot and sponge to absorb the water Courtesy U S Department of Agriculture



Fig 19—Stain Removal Applying a grease solvent Place fabric stained side down on a pad of absorbent material Sponge back of stain with pad dipped into grease solvent Apply only a little solvent at a time Work from center of stain toward outside edge using light brushing or tamping motion Courtesy U S Department of Agriculture

Stain	<i>Methods of Removing Some Common Stains</i>
Alkali	Yellow discolorations from an excess or careless use of washing soda borex ammonia and strong alkali soaps are removed by washing in water or by treatment with a mild acid as lemon juice (citric acid) white vinegar (4 per cent acetic acid) and oxalic acid solution. Rinse repeatedly.
Blood	Fresh blood stains on wash goods are removed by soaking in cold water and then washing in lukewarm soap solution. Fresh stains on clothing silk and wool are sponged with warm water and then bleached with $H_2O_2$ if a trace still remains. Steaming removes any resulting water rings. Fresh stains on heavy materials such as blankets may be removed by applying a thick paste of uncooked starch paste and brushing it off as rapidly as discolored. Old blood stains are soaked in 1 per cent ammonia and then laundered.
Chocolate Coffee	Fresh stains on washable goods are removed by stretching the goods across a supporting structure (bowl) and allowing hot water to run through them. Wash in hot soap solution. If necessary use a chlorine bleach. Fresh stains on unwashable goods are sponged with warm water. Any remaining grease spot from the cream used may be removed by a grease solvent as Carbons and naphtha.
Cod Liver Oil	Soak in kerosene one hour. Boil in soap solution ten minutes and rinse in warm water.
Cosmetics	Lipstick, nail polish and rouge may frequently be removed by ordinary washing. Any remaining stains can be dissolved by Carbons or acetone, to be followed by a chlorine bleach which is warm.
Egg	Scrape off as much egg as possible. Wash or sponge the goods with lukewarm water. Launder wash goods in warm soap solution. Any remaining grease spots are removed by grease solvents.
Fruit (dyes)	Fresh fruit stains on washable goods are usually soluble in running cold or hot water. A 50 per cent alcohol solution will generally remove fruit stains from silk or wool. Stains from fresh fruit are harder to remove than those from cooked fruits. Stains from dark fruits are difficult to remove and are set by soap. Lemon juice or a chlorine bleach on the goods and exposure to the sun will bleach most stains.
Grass	Wash and rub washable goods in cold water. For clothing silk or wool sponge with 50 per cent alcohol. A chlorine bleach will remove grass stains.
Grease (milk cream)	Grease spots with the exception of dark grease stains are removed by (a) Laundering wash goods (b) Using grease solvents (naphtha Carbons ether benzol) on goods over a blotter or towel and working from the outside of the spot toward the center (c) Using dry absorbents (starch French chalk, talcum powder) work in absorbent and when gummy, brush off and repeat again.

Stain	<i>Methods of Removing Some Common Stains</i>
Ink (ordinary)	When fresh most inks are soluble in running cold water in sweet milk (colored goods) in sweet or sour milk (white goods) in lemon juice salt mixture expose to the sun Fresh or old ink stains may be removed by the chlorine bleach or permanganate method
Iodine	Soap water ammonia solution and rinsing in hot water removes iodine Alcohol removes iodine from the skin.
Meat juice	Same methods as for blood
Mercurio- chrome	Washed out by regular laundry methods Alcohol containing a drop of $\text{HNO}_3$ or 'hypo' will remove Mercuriochrome from the skin
Mildew	Launder and dry in the sun or try the milk and lemon juice salt methods as in the case of inks
Paint (varnish tar and shellac)	Sponge fresh spots with paint solvents (turpentine naphtha benzol) Almost dry spots on washable goods may be softened with lard or butter and then removed by washing and rubbing in a warm soap solution Shellac is soluble in 60 per cent alcohol
Picric Acid	Boil in dilute sodium hydroxide solution for 30 minutes and then follow with a chlorine bleach
Rust	Lemon juice salt mixture (see inks) warm oxalic acid solution chlorine bleach
Salad	For a salad dressing containing eggs and cream sponge with warm water For a vinegar or lemon dressing wash in cold water then in soap solution and finally rinse in any fat solvent (naphtha) if an oil spot remains
Scorch	Scorches on linen or cotton may frequently be removed by rubbing with soap and water or moustening with water and exposing to the sun Scorched wool and silk may seldom be removed Sand peeping or rubbing a scorch on woolen goods and then sponging with hydrogen peroxide often removes slight scorched spots
Silver Salts	Sodium thiosulfate (hypo) removes silver stains if not too old Also some silver stains may be removed from the skin by first treating with iodine and then with dilute ammonia water
Tea	For wash goods boil in strong soap solution Sponge wool and silk Sometimes a stain may be removed by moustening with water working borax into the stain allowing to stand a few minutes and then rinsing in boiling water
Varnish	Sponge with acetone
Vaseline	Hot water sets Vaseline spots. Turpentine is a solvent for Vaseline Remove turpentine with a grease solvent



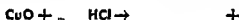
ride gas. Remove and touch the end of the glass rod to a piece of blue litmus paper. Result?  
This solution is hydrochloric acid.

(e) **ACTION ON A METAL:** Pour a few milliliters of dilute\* hydrochloric acid on about 1 cm. strip of magnesium ribbon contained in a test tube. Loosely close the mouth of the test tube with your thumb to collect and prevent the escape of the gas formed. In about a minute, remove your thumb and quickly bring the mouth of the test tube to a flame. Result?  
This gas is hydrogen. What replaced the hydrogen in the acid?



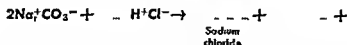
(f) **ACTION ON OXIDES OF METALS:** Barely cover the bottom of a test tube with copper oxide. Add 3 ml. of concentrated HCl. Carefully heat to boiling, and then fill the test tube with water. What evidence is there that a chemical action took place?

Complete the following equation:



(g) **ACTION ON HYDROXIDES** See Exercise 15.

(h) **ACTION ON CARBONATES:** Try the action of a few drops of any acid such as dilute hydrochloric acid upon a pinch of any carbonate, as sodium carbonate. Result?



(i) Summarize the characteristic properties of water solutions of acids, keeping in mind the typical acid, hydrochloric acid.

\* Dilute acid solutions for laboratory use may be made by adding one part of acid to approximately four parts of water.

**EXERCISE 14—CHAPTER VII**  
**TESTS FOR NONMETALLIC IONS**  
**(ELECTRONEGATIVE IONS)**

Section	Date	Name
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**MATERIALS** Sodium carbonate, solutions of silver nitrate, barium chloride, ferrous sulfate (saturated), potassium bromide, potassium iodide, ammonium molybdate, ammonium oxalate, disodium hydrogen phosphate, calcium chloride, and Rochelle salts. Chloroform, chlorine water (prepare chlorine water by pouring a few drops of hydrochloric acid on two or three crystals of potassium chlorate in a test tube. Then when the test tube is filled with green chlorine gas, fill the test tube one fourth full of water, close with the thumb, and shake it.)

The following tests are to stimulate an interest in qualitative analysis, and to develop certain technics:

(a) **CHLORIDE:** To 5 ml. of dilute hydrochloric acid in a test tube add sufficient silver nitrate solution to produce a heavy precipitate. Shake the mixture to coagulate the particles of silver chloride. When most of the precipitate has settled pour off the liquid above it, nearly fill the test tube with water, shake, and allow the precipitate to settle. Pour off the liquid as before and divide the precipitate equally among three test tubes.

1. To one portion add dilute nitric acid, and record whether the precipitate is soluble.

2. To the second portion add dilute ammonium hydroxide; shake the tube and record whether soluble.

3. The third portion when placed in a bright light, preferably sunlight for several minutes, turns

(b) **SULFATE:** To 5 ml. of dilute sulfuric acid in a test tube add barium chloride solution. The solid which separates is barium sulfate. Test its solubility in dilute HCl. Result?

(c) **NITRATE:** Pour into a test tube 3 ml. of saturated solution of ferrous sulfate. Add to it an equal quantity of very dilute nitric acid (5 drops of concentrated acid in 10 ml. of  $H_2O$ ). When the two solutions have been thoroughly mixed, incline the test tube



and carefully pour in 3 ml. of concentrated  $\text{H}_2\text{SO}_4$  in such a manner that the acid forms a separate layer. The brown coloration between the two layers of liquid constitutes the ring test for a nitrate.

(d) **BROMIDE:** To a solution of potassium bromide add about 1 ml. of chloroform and then a few drops of chlorine water.\* Place your thumb over the end of the test tube and shake vigorously. What is the color of the chloroform layer?

(e) **IODIDE:** Repeat the bromide test, using a solution of potassium iodide instead of potassium bromide. What is the color of the chloroform layer?

(f) **PHOSPHATE:** Add several drops of a solution of ammonium molybdate and a like amount of concentrated nitric acid to a solution of disodium hydrogen phosphate. Warm and allow to stand. What is the color of the precipitate?

(g) **CARBONATE.** Dissolve a pinch of sodium carbonate in 10 ml. of water. Have a drop of limewater ready on the end of a glass tube, add a few drops of dilute hydrochloric acid, and immediately, while the action is going on, hold the end of the glass tube just above the solution for a short time. Examine the limewater carefully in a bright light. What do you observe?

(h) **OXALATE** Add a few drops of calcium chloride solution to an ammonium oxalate solution. What result do you obtain?

(i) **TARTRATE:** To a solution of Rochelle salt, add several drops of silver nitrate solution. Result?  
Add dilute ammonium hydroxide a drop at a time, shaking after each addition, until the precipitate is nearly all dissolved. If the precipitate dissolves, a drop or two of silver nitrate solution will reproduce the precipitate. Warm the solution. What is produced on the sides of the test tube?

**Instruction:** Clean test tube used in (i) with a few drops of nitric acid.

\* If not provided on supply table refer to materials for method of preparing your chlorine water.

## SUMMARY

<i>Negative Ions</i>	<i>Reagent Added</i>	<i>Result</i>
Chloride		
Sulfate		
Nitrate		
Bromide		
Iodide		
Phosphate		
Carbonate		
Oxalate		
Tartrate		

If time permits, identify the acid radical in an unknown compound.

## EXERCISE 15—CHAPTER VIII

### BASES

Section	Date	Name
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**MATERIALS** *Dilute solutions of copper sulfate, ferric chloride, and magnesium sulfate sodium, lime (calcium oxide), litmus paper, 1 per cent phenolphthalein solution in alcohol*

(a) **PROPERTIES** Place separately in test tubes 5 ml portions of very dilute sodium hydroxide solution, very dilute ammonium hydroxide, and calcium hydroxide solution. Drop red litmus paper in each solution. Result?

Taste a drop of each solution. Result?

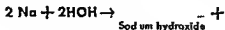
Write the formulas of the bases \_\_\_\_\_, \_\_\_\_\_,

In what respects are they similar in composition?

Pour 5 ml of sodium hydroxide solution in a test tube containing an equal quantity of a dilute acid, as hydrochloric acid. Feel the test tube. Is there an evidence of chemical action?



(b) **ACTION OF ACTIVE METALS ON WATER:** Remove the oil from a piece of sodium about as large as a grain of rice by pressing between filter papers. Throw it into an evaporating dish half full of water. Watch the action through a piece of glass or by standing at some distance to avoid being hit by the spattering drops. Consider that sodium displaces only one-half the hydrogen in water and complete the equation.



When active metals like sodium react with water what gas is liberated?

When the action is over describe the sensation of touch that a soluble hydroxide produces between your thumb and fingers

Touch a finger to the tongue. Neglecting the oily taste, what is its taste?

What is the effect of the solution on pieces of red and blue litmus paper?

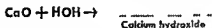
Add a few drops of phenolphthalein solution. What happens?

The substance contained in the water is sodium hydroxide. It is a typical strong base or alkali.

Summarize the characteristic properties of bases as observed in (a) and (b).

(c) ACTION OF THE OXIDES OF SOME METALS ON WATER: Place a piece of fresh lime as big as a marble in a small beaker and pour upon it about 5 ml. of water. What happens after it has stood about ten minutes?

The substance so formed is calcium hydroxide. It is commonly called slaked lime, and is much used by masons and plasterers. Write an equation, showing how calcium hydroxide is formed from calcium oxide and water.



(d) INSOLUBLE BASES BY PRECIPITATION. Place 2 ml. of copper sulfate, ferric chloride, and magnesium sulfate solutions in separate test tubes and dilute each with water to 10 ml. Add a few drops of sodium hydroxide solution to each solution and note the precipitation of the insoluble bases,  $\text{Cu(OH)}_2$ ,  $\text{Fe(OH)}_3$ , and  $\text{Mg(OH)}_2$ . Write equations for their formation.



Insoluble bases have no taste and no effect on the fingers or on indicators that is appreciable. They react with acids, however, just as soluble bases do.

**EXERCISE 16—CHAPTER VIII**  
**TESTS FOR METALLIC ELEMENTS**  
**(ELECTROPOSITIVE IONS)**

Section      Date      Name      ...

**MATERIALS** *Solutions of sodium chloride, potassium chloride, calcium chloride, copper chloride, mercurous nitrate, mercuric nitrate, ferric chloride, magnesium sulfate, ammonium oxalate, silver nitrate, potassium sulfocyanate, ammonium chloride, disodium hydrogen phosphate, platinum wire, copper chips or wire, lancet*

The following tests are to stimulate an interest in qualitative analysis, and develop certain technics.

**1. FLAME TESTS:** (These may be demonstrated.)

(a) Clean the wire by repeatedly dipping the end in concentrated hydrochloric acid and heating in the flame until the end of the wire imparts no color to the flame. It may be necessary to repeat this operation several times

(b) In making a test just touch the *end* of the wire to a drop of the salt solution, and heat in the edge (oxidizing part) of the flame.

(c) Place a drop of each of the solutions of sodium, potassium, calcium, and copper salts on a glass plate

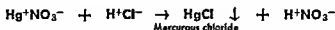
(d) Make the flame test with the sodium salt. *Clean the wire as before and test salts of potassium, calcium, and copper. Record results*

<i>Solution</i>	<i>Formula</i>	<i>Color of Flame</i>
1 Sodium chloride		
2 Potassium chloride		
3 Calcium chloride		
4 Cupric chloride		

**2. COLOR AND PRECIPITATION TESTS:** Use approximately 2 ml of the solutions of the following metallic salts, *e. g.*, take 2 ml. of a

solution of a mercurous compound to make the test for mercurous mercury.

(a) *Mercurous Salts.* Upon addition of dilute hydrochloric acid

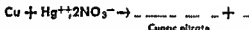


a precipitate forms which turns upon addition of sufficient ammonium hydroxide. Calomel is mercurous chloride. Will hydrochloric acid produce a precipitate with

a mercuric salt solution? Mercuric chloride is commonly called bichloride of mercury or corrosive sublimate.

Bichloride of mercury as compared to calomel is in water.

(b) *Mercuric Salts:* Drop a clean chip or a piece of copper into either the mercurous or mercuric salt solution. It will become silvered in a short time.



(c) *Iron Salts:* A few drops of potassium sulfocyanate solution added to 5 ml. of any ferric salt solution produces a color. If a ferrous salt is used it must be oxidized by boiling with a few cubic centimeters of nitric acid before making the test. Boil gently 2 ml. of nitric acid containing one drop of blood until a light yellow color is produced. Cool and dilute with an equal volume of water. Make the test for iron. Do you find iron in the blood?

(d) *Copper Salts.* Ammonium hydroxide added to a cupric salt solution forms a light blue precipitate which dissolves in an excess of the reagent to produce a colored solution. The flame test for copper is .

(e) *Magnesium Salts:* Add a clear mixture of 1 ml each of ammonium chloride, ammonium hydroxide, and disodium hydrogen phosphate solutions to 5 ml. of a magnesium salt solution. Allow to stand for several minutes. What is the color of the precipitate that forms on the inside of the test tube?

If calcium as well as magnesium is present in urine, the calcium must first be removed by the method in (f).

(f) *Calcium Salts:* Ammonium oxalate solution added to a calcium salt solution produces a \_\_\_\_\_ precipitate. By the flame test, the color of calcium compounds is \_\_\_\_\_.

(g) *Silver Salts:* Dilute hydrochloric acid added to a silver salt solution produces a \_\_\_\_\_ precipitate, which (upon vigorous shaking) in ammonium hydroxide  
If time permits, identify and record the metal found in an unknown compound

**EXERCISE 17—CHAPTER VIII****HYDROGEN ION-HYDROXYL ION CONCENTRATION**

Section	Date	Name
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**MATERIALS** *Alkacid or Nitrazine test papers solutions of material available as listed under A (c) N/10 HCl urine buffer mixture (Sorensen's pH 6.98 made by mixing 60 ml M/15  $\text{Na}_2\text{HPO}_4$  anhydrous 9.473 Gm per liter with 40 ml M/15  $\text{KH}_2\text{PO}_4$  9.078 Gm per liter)*

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**Instruction**

The principle of making hydrogen ion concentration (pH) measurements in terms of their pH notations is based on the fact that various chemical substances, known as "indicators" change color when they are acted on by solutions of different acidities or alkalinities. Test papers carrying a mixture of several indicators that are more sensitive than litmus are simple and inexpensive methods of making approximate pH determinations. Alkacid test paper made by Fisher Scientific Company makes pH measurement of liquids within a range of pH 2.0 to pH 10.0 with an accuracy of  $\pm 1\text{pH}$ , while Nitrazine test paper, made by E. R. Squibb and Sons, has a range of colors for pH 4.5 to 7.5 by half units. The Nitrazine is more accurate for acid determinations, but the Alkacid has a wider range. The use of both papers requires the same method of procedure.

**A TEST PAPER METHOD (APPROXIMATE\* pH)**

(a) **METHOD OF PROCEDURE** Dip a clean glass rod into the solution to be measured and transfer a drop to the surface of the paper, spreading it evenly by stroking. At the end of a minute compare the color produced with the standard color chart showing the various pH values (found on the container of the test papers).

(b) **ALTERNATE METHOD OF PROCEDURE** Dip paper into the solution three consecutive times and then shake off the excess liquid. At the end of a minute compare color of paper with colors on chart.

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\* The accuracy of colorimetric methods is affected by salts, proteins, colloids, temperature, oxidation, reduction, slightly buffered solutions—any one of which produces specific errors of 0.5 pH units or more. For great accuracy, electrometric methods are used.



(c) **DETERMINATIONS AND TABULATION:** Determine and record in the table the pH values of the solutions and physiological material available.

<i>Material to be Tested</i>	<i>Approximate Values</i>	<i>pH Values Found</i>
Human blood plasma	7.3-7.5	
Adult gastric contents	0.9-1.6	
Saliva.	6.0-7.6	
Urine (human)	4.8-8.0	
Milk, cow's	6.2-7.3	
Milk of magnesia	10.5	

### B. BUFFER ACTION

A number of substances exert what is known as buffer action. This means that considerable amounts of acid or alkali can be added to solutions of these substances, or that the solutions can be diluted, with only a relatively small change in the pH values.

(a) **EFFECT OF A BUFFER ON pH MEASUREMENTS:** To 10 ml. of distilled water which has a pH of about 6.0, add one drop of N/10 HCl. What is the approximate change in pH value?

Now to 10 ml. of buffer mixture pH 7.0, add one drop N/10 HCl. What, if any, is the change in pH value? Add N/10 HCl drop by drop until a definite change in pH value is obtained.

Add a drop of N/10 HCl to a specimen of urine. Is the change in pH value greater than the change with the buffer mixture? Is the change as great as the change in water alone?

(b) **EFFECT OF DILUTION ON pH VALUES:** Dilute a buffer mixture and a specimen of urine with the same amount of water. Make pH determinations of each solution

What is the degree of dilution necessary to cause a change in pH value?

## EXERCISE 18—CHAPTER IX

### NEUTRALIZATION: HYDROLYSIS

Section	Date	Name
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**MATERIALS** Sodium hydrogen carbonate, phenolphthalein indicator, sodium carbonate, ammonium chloride, blue litmus paper

#### A. NEUTRALIZATION

(a) The mixing of a base and an acid solution in the exact quantities for complete reaction with each other is called neutralization and the products formed are salt and water. How could you determine by means of litmus paper whether a solution was exactly neutral?

(b) Dilute about 2 ml. of sodium hydroxide solution with an equal volume of water. To this solution in an evaporating dish add a few drops of dilute hydrochloric acid and one small piece of litmus paper. Stir the resulting solution with a glass rod and continue to add the acid drop by drop until the resulting solution is neutral, i. e., a drop of acid or base will cause the piece of litmus paper to change color, or is at most very slightly acid. Considering that the characteristic properties of an acid are due to the hydrogen ions,  $H^+$ , and those of a base due to the hydroxyl ions,  $OH^-$ , then if the solution is neutral, that is, neither acid nor basic, what new undissociated molecule is always formed in neutralization?

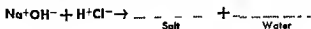
Remove the litmus paper and drop it into the waste jar, not in the sink.

Evaporate the solution to dryness. Taste the residue. Result?

What is it?

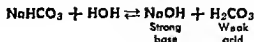
What is the name given to any compound formed by the interaction of any acid and any base?

Complete the following ionic equation, showing that an ionized salt and undissociated water are formed in neutralization



# B. HYDROLYSIS OF SALTS

(a) A salt formed from a strong base and a weak acid. Dissolve about 1 gram (curved portion of test tube) of sodium hydrogen carbonate (baking soda) in half a test tube of water.



Add to this solution one drop of phenolphthalein indicator. Is the solution acid or alkaline? In hydrolysis both a base and an acid are formed, one of which may be stronger than the other. Why is this solution alkaline?

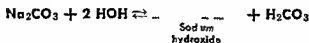
How do you account for the bitter taste sometimes present in baked biscuits and cakes?

Set aside the pink solution for comparison with (b).

(b) Heat approximately the same weight (1 Gm) of dry sodium hydrogen carbonate in an evaporating dish with an occasional stirring for ten minutes.



Cool and dissolve this residue in half a test tube of water.



Add one drop of the indicator and compare the depth of color with that obtained with (a).

Which compound, the  $\text{NaHCO}_3$  or the heated  $\text{NaHCO}_3$ , that is the  $\text{Na}_2\text{CO}_3$ , hydrolyzes the more?

Dissolve in one-half test tube of water approximately the same weight (1 Gm) of sodium carbonate (washing soda) obtained from the supply table, and compare the taste of this solution with the taste of the solution of salt just prepared from the heated sodium hydrogen carbonate. Result?

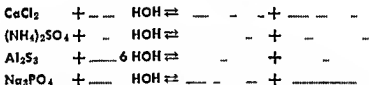
State the household name of the compound formed by heating baking soda

(c) *A salt formed from a weak base and a strong acid* Dissolve a few crystals of ammonium chloride in half a test tube of water. Insert a piece of blue litmus paper. Remove the litmus paper. The color of the litmus paper indicates that this salt, ammonium chloride, forms an \_\_\_\_\_ solution



The results from (a), and (b), and (c) indicate that some salts in solution give acid or alkaline reactions. This is a special type of reaction involving water, called *hydrolysis*, and is the result of a reaction between the salt and water with the formation of an acid and a base, one of which is more dissociated than the other. When equations of hydrolysis are read in reverse they become examples of

(d) Complete the following hydrolysis equations



Considering that natural water contains some calcium chloride what effect will such waters have on iron pipes or boilers?

## EXERCISE 19—CHAPTER IX

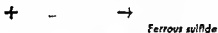
### METHODS OF PREPARING SALTS

Section      Date      Name

**MATERIALS** Sodium hydrogen carbonate, quinine, solutions of lead acetate sodium sulfate, magnesium sulfate, quinine sulfate (1 500), tea coffee, tannic acid, picric acid, iodine (in KI), potassium permanganate, phenolphthalein  
Optional solutions will be found on p 692

#### A. SOME METHODS OF PREPARING SALTS

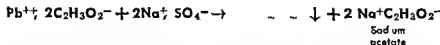
(a) **DIRECT COMBINATION** Recall the second experiment of iron and sulfur in Exercise 2 Write the equation



(b) **NEUTRALIZATION.** Recall the experiment just performed in this chapter on neutralization Write the equation



(c) **PRECIPITATION \*** To a test tube containing a few milliliters of lead acetate solution, add sufficient sodium sulfate solution to produce a precipitate Considering that all sodium salts are soluble, name the precipitate formed

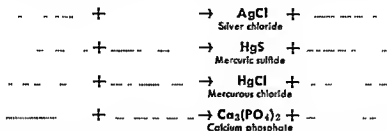


Could Epsom salts ( $\text{Mg}^{++}\text{SO}_4^{--}$ ) be used instead of sodium sulfate (Glauber's salt) to precipitate the lead ion?

In the preparation of an insoluble salt from the action of two soluble salts, how can the soluble salt formed be recovered?

\* This experiment is to arouse an interest in constructive work, familiarize the student with the solubility table and to show the practical value of knowing how to form in soluble compounds For instance some poisonous compounds may be rendered harmless by changing them over into insoluble compounds

Consult the solubility table, p. 778, and select soluble salts for the formation of the following *insoluble* salts



(d) **VOLATILITY:** Cover the bottom of a test tube with baking soda and add dilute hydrochloric acid drop by drop until you can see that no more gas is being evolved. Evaporate and taste the residue. What is it?



(e) **GENERAL METHODS OF PREPARING SOLUBLE SALTS:** Write equations for the action of an acid upon a metal, a metallic oxide, a hydroxide, and a carbonate.



### B. ALKALOIDS

(a) **SOLUBILITY:** To a very small amount, the size of a pinhead, of quinine alkaloid (not the salt) in a test tube add a few milliliters of water. Agitate it. Is it soluble? Now add a drop of sulfuric acid. Warm and agitate it. Result?

Alkaloids combine with acids to form salts. Considering this, which are water soluble, the pure alkaloids or the alkaloid salts?

(b) **TASTE:** Taste a few drops of the quinine sulfate. Result?

(c) **REACTION:** Into a test tube containing about 5 ml of distilled water, add a small amount (size of grain of rice) of quinine alkaloid (not the salt). Shake the tube thoroughly and test with a drop of phenolphthalein solution. Look down through the liquid in the test tube. Any color change? What does this indicate concerning the nature of an alkaloid?

(d) Summarize the common characteristic properties of alkaloids, using quinine as an example

(e) **PRECIPITANTS:** Into test tubes, each containing about 5 ml of quinine sulfate solution, add separately one or more drops of tea, coffee, tannic acid, picric acid, iodine, and potassium permanganate solutions. Record results in the following table

<i>Solutions of</i>	<i>Action on Alkaloid</i>
Tea	
Coffee	
Tannic acid	
Picric acid	
Iodine	
Potassium permanganate*	

\*Potassium permanganate ( $\text{KMnO}_4$ ) oxidizes the alkaloid to a harmless compound

Why can tea be used as an antidote in alkaloid poisoning?

If so directed by the Instructor test and record the action of the following "alkaloidal reagents" on 5 ml. portions of quinine sulfate solution.

<i>Solutions of</i>	<i>Action on Alkaloid</i>
Potassium mercuric iodide (Mayer's reagent)	
Phosphomolybdic acid	
Phosphotungstic acid	



## EXERCISE 20—CHAPTER X

### AMMONIA

Section      Date      Name      .

MATERIALS: *Ammonium sulfate, slaked lime, ammonium chloride*

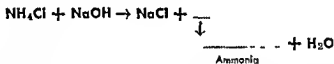
(a) Place a pinch of ammonium sulfate in the hand and smell. Smell a pinch of dry, slaked lime,  $\text{Ca}(\text{OH})_2$ . Rub the two together in the palm of the hand. Smell. Result?

Bring a moistened strip of red litmus paper near the mixture. Result?

Indicates what? ..

(b) Repeat (a), using ammonium chloride and slaked lime,  $\text{Ca}(\text{OH})_2$ . Results?

(c) Heat gently in a test tube a small amount of ammonium chloride with any strong hydroxide solution, as sodium hydroxide. Smell. Result?



How may you prove that any substance given you is or is not an ammonium salt?

(d) What kind of a substance have you used each time to free ammonia from ammonium compounds? What general method of preparing ammonia is indicated by these experiments?

(e) What is the odor of ammonia? Is it heavier or lighter than air?

(f) To a test tube one third full of water add one drop of *dilute* ammonium hydroxide (1 5) Heat to boiling and smell Result?

Continue the boiling for *several minutes* (five) Smell What must have happened to the compound dissolved in the water?

How does heat affect its solubility in water?

What do you conclude about the stability of ammonium hydroxide?

(g) Tabulate the differences between ammonia and ammonium

	<i>Ammonia</i>	<i>Ammonium</i>
Formula		
Free or combined		
Gas or radical		
Exists in water as		

If time permits, obtain an unknown substance from the Instructor and test it to determine if it is an ammonium salt

**EXERCISE 21—CHAPTER X**  
**CHLORINE**

Section      Date      Name

MATERIAL: *Potassium chlorate*

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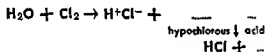
To a few crystals of potassium chlorate in a dry test tube add several drops of concentrated hydrochloric acid.

(a) The color of the gas (chlorine) formed is

(b) Cautiously smell    Result?

(c) Hold a piece of dry red litmus paper and a piece of moist red litmus paper in the mouth of the test tube for a few seconds only.

What happened to the moist red litmus paper?



Hold a piece of moist blue litmus paper in the mouth of the test tube of chlorine gas

The first color change in the blue litmus is due to the presence of what ions?

The second change in color is due to

(d) Half fill the test tube with water, close the mouth with your thumb, and shake. Make an ink spot on a piece of paper and immerse in the liquid. Allow to stand. Result?

What practical application can be made of this kind of a solution?

## EXERCISE 22—CHAPTER X

### IODINE

Section                  Date                  Name

**MATERIALS** *Potassium iodide, manganese dioxide, dilute sulfuric acid (two to one), ethyl alcohol, 1 per cent cooked starch solution, dilute (5 per cent) sodium thiosulfate solution*

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(a) **PREPARATION:** Into a dry test tube add 1 Gm. (curved portion of the bottom of a test tube) of powdered potassium iodide and an equal bulk of manganese dioxide. Mix carefully so that none will adhere to the side of the test tube. Now add 3 ml. of dilute sulfuric acid (two parts of acid to one part of water). Holding the test tube at an angle, warm the *lower* end of the tube very gently. The upper end of the test tube must be kept as cool as possible if iodine crystals are to be formed by condensation. Note the vapor of the iodine and the grayish black crystals which deposit near the mouth of the tube. If the iodine starts to vaporize and escape from the test tube, hold an inverted test tube against the mouth of the heated test tube in order to condense and collect crystals of iodine.

(b) **PROPERTIES:** Using a wood splint or a glass rod, scrape out some of the crystals in the inside of the tube. Using about the same number of crystals in each case, test the solubility of iodine in the same amount (2 ml) of water, alcohol, and a solution of potassium iodide in water. Reserve these solutions.

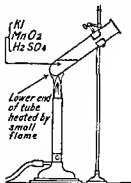


Fig 20

What name is given in pharmacy to the alcoholic solution of iodine just prepared?

How could you remove an excess of iodine from the skin?

<i>Solvent (2 ml )</i>	<i>Color of Solution</i>	<i>Degree of Solubility (slightly, moderately, or very)</i>
Water		
Alcohol		
Potassium iodide solution		

(c) **REMOVAL OF IODINE STAIN:** Divide the alcoholic iodine solution into two parts. To one add a few drops of ammonium hydroxide and to the other sodium thiosulfate solution. Result?

In both cases the iodine is changed into a colorless iodine solution. Either of the two procedures may be used in removing iodine stains from clothes.

(d) **STARCH TEST FOR FREE IODINE:** Add a drop of iodine in potassium iodide solution to a few ml. of dilute starch solution.

What color is produced?

What difficulty might be met with in attempting to remove iodine from starched cloth by the use of ammonium hydroxide or sodium thiosulfate solution?

## EXERCISE 23—CHAPTER X

### PROPERTIES OF CARBON

Section      Date      Name

**MATERIALS** *Litmus solution, powdered copper oxide, limewater, powdered wood and animal charcoal*

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(a) **DECOLORIZER** Dilute some blue litmus solution in a test tube with enough water to give it a light color. To one-half of this solution in another test tube, add about 3 ml. of animal charcoal, shake, *warm carefully* two minutes and filter. Compare the color with that of the original solution. What happened to the litmus?

The coloring matters in vinegar, raw sugar, indigo, etc., belong to the same class of matter as litmus (colloidal substances), and these are removed by animal charcoal.

(b) **DEODORIZER**: Half fill a test tube with water and add enough ammonium hydroxide (two or three drops) to give a marked odor of ammonia. Next fill approximately half of the remaining space in the test tube with dry animal charcoal. Close the mouth of the tube with your thumb and shake thoroughly for two minutes. Smell. Is the odor as strong as the original solution?

(c) **REDUCING AGENT** Mix thoroughly 2 Gm. of powdered copper oxide with an equal amount of wood charcoal in a test tube. Fit the test tube with a delivery tube extending into a test tube

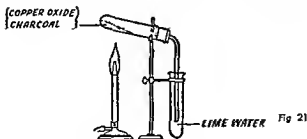


Fig 21

half filled with limewater. Heat for ten minutes. What has happened to the limewater?

Explain

Empty the contents of the test tube on a paper upon the desk. What is the reddish brown material?



To what process has the copper oxide been subjected?

What happened to some of the charcoal?

The above equation shows that carbon is a agent.

What kind of an agent is copper oxide?

Whenever there is reduction there simultaneously has to be

State three properties of carbon

**EXERCISE 24—CHAPTER X****CHANGES IN AIR CAUSED BY RESPIRATION**

Section	Date	Name
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**MATERIALS** *Deflagrating spoon, birthday candles, string or rubber band*

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Fill three bottles with water and invert them over water in trough.

(a) Using a glass tube, a rubber tube, or both, displace the water in one bottle with *beginning* expired air. Slip a glass plate under the mouth of the bottle, and stand it in an upright position on the table.

(b) Displace the water in the second bottle with air from the *end* of expirations, that is the last portions of air expelled from the lungs. Cover with a glass plate and stand right side up on the table.

(c) Take a big breath of air and hold it in the lungs for half a minute, if possible, and then displace the water in the third bottle with the *beginning expired* air.

(d) Fasten a candle to a deflagrating spoon with a rubber band or string. Light the candle, slip aside the cover glass on the first bottle, and lower the burning candle. In a similar way, test the air in the other two bottles. From the behavior of the candle flame in the first and second bottles, what conclusion may be drawn concerning the amount of oxygen in the last portions of ordinary expired air?

Why is this so?

How do the *first portions* of expired air held in the lungs for half a minute compare in oxygen content with the *end portions* of ordinary expired air?

What is the effect of deep respiration upon the percentage of oxygen in the expired air?

What is the effect of deep respiration upon the percentage of carbon dioxide in the expired air?

(e) What is the function of carbon dioxide in the oxygen-carbon dioxide mixture used in suffocation, collapse, or recovery from anesthesia?



## EXERCISE 25—CHAPTER XII

### DESTRUCTIVE DISTILLATION

Section      Date      Name

**MATERIALS** *Lead acetate solution, wood splints, soft coal, five-inch test tube with side arm and connection c (Fig 22)*

#### A. DESTRUCTIVE DISTILLATION OF WOOD

1. Break six or seven wood splints in the middle and place in the lower part of the test tube. Set up apparatus according to accompanying figure, with mouth of test tube slightly lower than the other end. Why?

Heat gently at first and then strongly until no further change is noted. During the heating, occasionally bring a flame to the edge of the jet tube. Result?

Is the flame luminous?

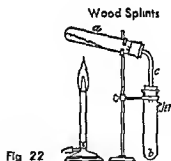


Fig 22

2. Test the liquid in the test tube (b) with blue litmus paper. Result?

What name is given to the substance that causes this change?

3. What other liquids are present in the test tube (b)?

- 4 Remove, examine, and name the residue left in the glass test tube (a)
- 5 What three main commercial products are obtained by the destructive distillation of wood?
- 6 State an important use of each product formed

### B DESTRUCTIVE DISTILLATION OF SOFT COAL

1 Fill a glass test tube (same one used in A), one half full of coarsely ground soft coal, forming a layer on the lower side of the test tube. This allows space above the coal for expansion. Place a piece of filter paper moistened with lead acetate solution on the inside of the test tube (b), Fig 23, the end projecting from the mouth of the tube so that it will be held in position by the stopper when inserted. Heat gently at first and then strongly until no further change is noted.

2 Test the gas at the end of the jet with a flame. Result?

Does it act similar to illuminating gas?

3 What compound is formed on the filter paper, considering that hydrogen sulfide is in the gas?

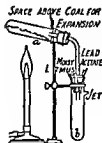


Fig 23

4. What liquid collects in the test tube (b)?

Remove the stopper from the tube (b), add about as much sodium hydroxide solution as there is liquid in the tube, warm gently and at the same time hold a piece of moistened red litmus paper at the mouth of the tube. Considering that the coal contains nitrogen, what volatile gas formed would turn moist red litmus paper to a blue color?

5. What is the residue left in test tube (a)?

6. What main products are obtained by the destructive distillation of soft coal?

Are the substances identified of importance commercially?

State an important use of each product formed

**EXERCISE 26—CHAPTER XII****COMPOSITION OF MOST ORGANIC COMPOUNDS**

Section	Date	Name
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**MATERIALS** *Dry egg albumin, casein, powdered copper oxide, soda lime, sodium, solution of lead acetate, ammonium molybdate solution, granular copper oxide, sodium chloride*

*For optional methods Five-inch small bore glass tubing, powdered copper oxide, sugar, soda lime ( $\text{CaO} + \text{NaOH}$ ), ferrous sulfate solution containing a trace of ferric chloride, sodium nitroprusside solution (fresh), platinum wire*

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**Instruction:**

*Carbon, hydrogen, and oxygen with occasional smaller amounts of nitrogen, halogens, sulfur, and phosphorus are the chief elements found in organic compounds.*

(a) **CARBON AND HYDROGEN** Organic compounds are frequently flammable, and when heated take fire or char. Carbon and hydrogen are detected by oxidation

1. Heat a very small amount of dry egg albumin (or casein) in a test tube held in an inclined position. What does the change in color of the organic compound indicate?

What collects in the upper and cooler portion of the test tube?

Continue the heating until there is no further change. The charring indicates the presence of \_\_\_\_\_, while the formation of water indicates the presence of \_\_\_\_\_

Complete oxidation of organic compounds releases energy and forms what two main products?

2. *Optional:* A more delicate test for carbon is to heat the substance with some easily reducible metallic oxide, the oxygen of which unites with the carbon to form carbon dioxide. The presence of the carbon dioxide may be shown by passing the gas through limewater. Hydrogen is at the same time oxidized into water, which condenses on the cold part of the apparatus.

Take a piece of a small bore soft glass tube about five inches long and fuse it together at one end. Mix in a mortar a pinch of fine

copper oxide with about one-tenth of its bulk of powdered sugar. Pour the mixture into the tube and bend it so as to form a right angle. Let the open end dip into limewater contained in a test tube (Fig. 24). Heat the mixture gently with a small flame. The

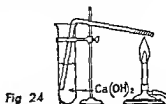
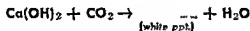
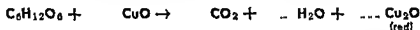


Fig 24

gas which bubbles through the limewater turns the limewater  
 , thereby indicating that carbon was oxidized  
 to , which reacted with the limewater to  
 form . Moisture soon appears on the sides  
 of the tube. Considering that the oxygen came from the copper  
 oxide, the formation of water indicates the presence of  
 in the compound.



Gases or volatile substances like ether and alcohol cannot, of course, be examined in this way, but the gases or liquids may be burned in a closed vessel, or the vapor led over a layer of red-hot copper oxide and then through limewater.

(b) NITROGEN: Organic compounds containing nitrogen evolve ammonia upon being heated with soda lime.

1. Mix thoroughly a small amount of dry egg albumin (or casein) with an equal bulk of soda lime. Place in a dry test tube and heat, at the same time holding a piece of moistened red litmus paper at the mouth of the tube. The formation of a blue color shows that the gas evolved, which forms a base with the moisture, must be

2. *Optional:* When nitrogenous organic compounds are heated with metallic sodium, sodium cyanide is formed, and the subsequent test is the same as for a cyanide.

Pour about 10 ml. of water in a beaker. Place a fragment of gelatin or cheese in a small, *dry* test tube along with a piece of metallic sodium the size of a grain of rice. Hold the test tube horizontal and beat the lower end at first gently, until the reaction subsides, and then strongly, until the glass is nearly red-hot. At this stage the carbon will have been mostly burned out of the nitrogenous substance, leaving a white to grayish ash in the test tube.

At arms' length (warning) place the hot end of the tube in the beaker containing 10 ml. of water. The glass crumbles away, and any residual sodium is decomposed with a bright flash; all the cyanide rapidly goes into solution, while a small quantity of carbon remains suspended in the liquid. Filter into a test tube. Pour into the clear solution about 1 ml. of ferrous sulfate solution to which a drop of ferric chloride has been added, boil for a minute, cool, and acidify carefully with a few drops of dilute hydrochloric acid. A colored precipitate indicates the presence of nitrogen.

(c) **SULFUR:** Loosely combined sulfur after being boiled with sodium hydroxide forms sodium sulfide, which gives a black precipitate with lead acetate solution.

1. To 2 ml. of dilute sodium hydroxide in a test tube add a very small amount of egg albumin (or casein), and heat for a minute or more, cool the test tube in running water, and then add a few drops of lead acetate solution. The formation of insoluble lead sulfide indicates the presence of sulfur. Repeat the experiment with hair.

2. *Optional: Sulfur* (loosely combined): The presence of sulfur in organic compounds may be detected by heating the substance with metallic sodium. The alkaline sulfide, when dissolved in water, gives a violet coloration with a solution of sodium nitroprusside.

Heat a fragment of egg albumin with a piece of sodium in a dry test tube until the bottom of the tube is red-hot, and place it in about 10 ml. of water in a beaker of water. Filter the liquid and add a few drops of sodium nitroprusside solution. What is the color?

(d) PHOSPHORUS: Upon oxidation, phosphorus changes to a phosphate, which with ammonium molybdate produces a yellow precipitate.

To a small amount of casein in a test tube add approximately 1 ml. each of concentrated nitric and sulfuric acids. Boil carefully until the solution becomes clear. Cool thoroughly, and then add slowly about as much cold water as you have liquid in the tube. Add a small amount of ammonium molybdate solution and warm

carefully. A precipitate indicates the presence of phosphorus. If a colored precipitate does not form, try the technic for a phosphate on page 677.

(e) HALOGENS: Many halogen compounds impart a green fringe to the outer mantle of the nonluminous flame. A more delicate test is to heat the substance with copper oxide, which gives a vivid green coloration.

Heat a fragment of granular copper oxide, held in the loop of a platinum wire, in the outer mantle of the nonluminous flame until it ceases to color the flame green. Let it cool down a little and then dust on some halogen compound. Now heat again. A bright flame, accompanied by a blue zone immediately around the oxide, indicates the presence of a *halogen*.

(f) OXYGEN: There are no satisfactory direct tests for oxygen, and it is almost invariably calculated by difference.

**EXERCISE 27—CHAPTER XII****SATURATED AND UNSATURATED OPEN-CHAIN  
HYDROCARBONS**

Section	Date	Name
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**MATERIALS:** *Fused sodium acetate, soda lime (sodium calcium hydrate), very dilute bromine water, 95 per cent ethyl alcohol, calcium carbide, sidearm test tube, medicine dropper, corks, small cylinder of ethylene (if available).*

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**Instruction:**

*The aliphatic or open-chain hydrocarbons are (1) saturated compounds, that is, they contain not more than two shared electrons between their carbon atoms, or (2) unsaturated compounds with four or six electrons shared between their carbon atoms. In performing the following experiments on the saturated hydrocarbons (represented by methane) and the unsaturated hydrocarbons (represented by ethylene and acetylene) look for differences between them in the degree of explosiveness when mixed with air, in the color of their flames, and in the type of reaction with bromine, i. e., whether they form substitution or addition products. All hydrocarbons undergo oxidation.*

With the consent of the Instructor, two students may work together on the following experiments. If time does not allow for completion of (a), (b), and (c), omit (b).

(a) **METHANE** Natural gas is approximately 90 per cent methane, and if available use it as a source of methane, otherwise make the methane as directed. Using a dry test tube, set up apparatus as in Fig. 25. Have ready a stoppered test tube. Fill the generator one-half full with a mixture of one part fused sodium acetate and two parts soda lime. Heat carefully, and after allowing some of the gas to escape, collect one half a test tube of methane gas. Lift the test tube from the water so that the water will run out of the test tube and air will rush in to mix with the methane. Close the mouth of the test tube with your thumb and bring the tube horizontally, to the side of a Bunsen burner flame. Remove your thumb.

**Result?**

Collect and stopper a test tube of methane. Remove the glass delivery tube from the water and ignite the escaping methane

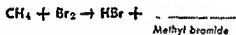


Does the color of the flame indicate that carbon is being liberated, *i. e.*, produces a colored flame?

Invert a clean, dry bottle for a few seconds over (not in) the Bunsen burner flame. Observe the film of moisture on the inside of the bottle. Add a few milliliters of limewater to the bottle. Close with a glass plate or rubber stopper and shake the bottle thoroughly. Result?

What are the products of complete combustion of hydrocarbons?  
and

To the stoppered test tube of previously collected methane, add a few drops of bromine water. Restopper and shake the tube vigorously. Does the bromine show any change in color? No change in color of the bromine water indicates no reaction. Thrust a glass rod, previously dipped into ammonia water, into the test tube. A white cloud of ammonium bromide indicates the presence of HBr gas. Complete the reaction



Is this type of reaction of a halogen with a saturated hydrocarbon (represented by methane) one of substitution or of addition?

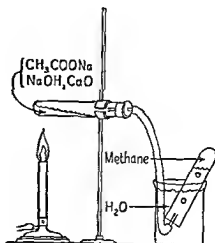


Fig 25—A Laboratory Method of Preparing Methane.

(b) **ETHYLENE:** (*The laboratory preparation of ethylene is difficult and an inefficient process. If available collect two test tubes of gas from the ethylene cylinder on the supply table. Otherwise in groups of two or three make the ethylene as directed.*) Use a dry sidearm test tube and a dry medicine dropper, the bulb of which must fit tightly. Set up an apparatus as in Fig. 26. Have ready two cork stoppered test tubes. Remove the rubber stopper containing the dry medicine dropper, and fill the dropper completely with ethyl alcohol. Place about 5 ml of concentrated sulfuric acid in the dry sidearm test tube, and with a very small flame carefully heat just to boiling. Replace the stopper and hold it in tightly during the collection of the ethylene, largely because of the danger of sulfuric acid spattering out of the tube when the alcohol falls on the hot acid, and by means of the medicine dropper, allow ethyl alcohol to fall, drop by drop, upon the hot sulfuric acid. Allow a few bubbles of gas to escape and then collect two test tubes of ethylene gas. In order to collect sufficient gas it may be necessary to keep the acid hot by gently heating it from time to time. If the experiment has to be repeated in order to collect more ethylene, remember that the generator tube must be dry before adding the concentrated sulfuric acid. Bring one tube of ethylene gas horizontally to the side of (not in) a Bunsen burner flame. Remove cork to ignite the gas.

Result?

How does the color of the ethylene flame compare with that of the methane flame?

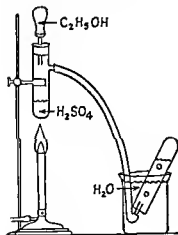
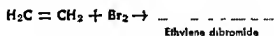


Fig 26—Making Preparation of Ethylene

Add a few drops of bromine water to the second test tube of ethylene, stopper, and shake it *vigorously*. Result?



From the equation would you expect to prove the presence of HBr? The decoloration of bromine with ethylene and the failure to prove the presence of HBr indicate that ethylene is an \_\_\_\_\_ compound

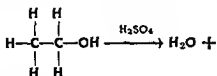
Is the dominant type of reaction of an unsaturated hydrocarbon (represented by ethylene) that of substitution or of addition?

Is the decoloration of bromine more rapid with saturated or unsaturated hydrocarbons?

Which type of hydrocarbon is the more reactive?

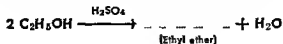
How many shared electrons are there between the carbon atoms of ethylene?

Complete the following equation for the preparation of ethylene:



Combustion of ethylene:  $\text{C}_2\text{H}_4 + \text{---} \text{O}_2 \rightarrow \text{---} + \text{---}$

Conditions such as temperature, pressure, and concentration greatly modify reactions. Thus ethylene is produced by the dehydrating action of sulfuric acid on ethyl alcohol, but at a temperature lower than  $150^\circ \text{C}$ . and with an excess of ethyl alcohol, the product formed is mostly ethyl ether (diethyl oxide).

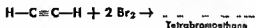


(c) **ACETYLENE** Use the same apparatus, excepting the burner, as in the preparation of ethylene. Have ready a stoppered test tube. Fill the curved portion of the *dry* test tube generator with small lumps of calcium carbide, and, by means of the medicine dropper, allow water to fall, *drop by drop*, upon the carbide. Allow a few bubbles of gas to escape and then collect one-half a test tube of acetylene gas. Lift the tube from the water and carry, mouth downward, to (not in) a flame. Result?

The acetylene-oxygen mixture is one of the most dangerous gaseous explosive mixtures known.

Collect a test tube of acetylene and quickly bring the mouth of the test tube to the *side* of a flame. What element is liberated when acetylene is incompletely burned? The color of the acetylene flame is characteristic of unsaturated compounds when burned in a limited supply of oxygen. In comparing the color of the flame of the three classes of hydrocarbons (methane, ethylene, acetylene) how does the unsaturated class differ from the saturated class (represented by methane) with respect to completeness of combustion?

Collect another test tube of acetylene, stopper, and shake vigorously with several drops of bromine water. Result?



The decolorization of bromine with acetylene gas, and the failure to prove the presence of HBr formation indicates that acetylene, like ethylene, is an \_\_\_\_\_ compound. Is the dominant type of reaction of an unsaturated compound (represented by acetylene) that of substitution or addition?

Is the decoloration of bromine more rapid with saturated or unsaturated hydrocarbons? What does that indicate?

Is acetylene more active than ethylene?

Complete the following equations:

Preparation of acetylene:  $\text{CaC}_2 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \dots$

Combustion of acetylene:  $\text{C}_2\text{H}_2 + \dots \text{O}_2 \rightarrow \dots + \dots$

### Differences Between Three Classes of Hydrocarbons

	<i>Methane</i>	<i>Ethylene</i>	<i>Acetylene</i>
Molecular formula			
Graphic formula			
Class (based on number of shared electrons)			
Explodes with air (slight, moderate, very)			
Color of flame			
Dominant reaction (substitution or addition)			
Order of activity (1st, 2nd, 3rd)			

## EXERCISE 28—CHAPTERS XIII AND XIV

### ALCOHOL, ALDEHYDES, ORGANIC ACIDS, ESTERS, AND ETHER

Section	Date	Name
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**MATERIALS** *Thermometer, glass condensing tube, compressed yeast, Karo syrup, camphor, oil, iodine crystals, dilute potassium dichromate solution, ethyl alcohol, methyl alcohol, copper spiral to fit in a test tube* (Use three feet of No. 14 copper wire. At a distance of three inches from one end wind the wire about 15 times around a pencil into a close spiral until within eight inches of the opposite end. Push the longest end through the coil and twist together to form a handle.)

*Resorcin solution (1 per cent), silver nitrate solution, formaldehyde solution, Benedict's solution (17.3 Gm. of copper sulfate, 173 Gm. of sodium citrate, and 100 Gm. of anhydrous sodium carbonate, made up to one liter with distilled water, Add the copper sulfate dissolved in 100 ml. of water slowly to about 800 cc. of the other filtered ingredients, and finally make up to a liter)*

*Tollen's solution* (Add  $\text{NH}_4\text{OH}$  to dilute  $\text{AgNO}_3$  solution until the precipitate which first forms dissolves), *Pasteur's salts* (860 ml. distilled water containing 2 Gm.  $\text{K}_2\text{PO}_4$ , 0.2 Gm.  $\text{Ca}_3(\text{PO}_4)_2$ , 0.2 Gm.  $\text{MgSO}_4$ , 10 Gm.  $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ )

*Acetic acid, amyl alcohol, saturated methyl alcoholic solution of salicylic acid, butyric acid, amyl acetate, milk, ferric chloride solution (5 per cent)*

### A. ALCOHOL

**NOTE** To be started several days before the regular laboratory period by student or instructor. The laboratory prepared alcoholic solution contains small amounts of esters, aldehydes, and higher alcohols.

**PREPARATION.** Dissolve one eighth cake of yeast in a flask containing 150 ml. of water, 20 ml. of Karo syrup, and 9 ml. of Pasteur's salts (for the yeast to feed on). Put in some warm place for several days. Decant the liquid into a flask leaving the sediment in the bottom of the fermentation flask. Save one half of a test tube for (c). Set up the apparatus similar to Fig. 27. Use approximately 150 ml. of the fermented solution previously prepared, and distill 5 to 10 ml. at as low a temperature as possible. The liquid should barely simmer, not boil. The temperature at which the liquid begins to distill is . . . ° C. Save the undistilled portion for part C, Organic Acids



(b) **PROPERTIES:** Record the odor and taste of the distillate

Apply a lighted match to a small portion in an evaporating dish.  
Result?

Oxidation of alcohol in the human body generates heat with the formation of two end products, namely                      and                      ..

In a test tube containing some of the distillate, test the solubility of some camphor or a drop of oil. Is the camphor or oil very soluble in cold alcohol?                      In boiling alcohol?

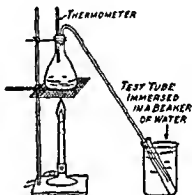


Fig. 27—Distillation Apparatus

(c) **TEST.** To a few milliliters of the alcohol add a few iodine crystals and shake it until a dark brown color is produced. Add sodium hydroxide solution a drop at a time until the dark brown color changes to a deep yellow. Iodoform separates as a yellow precipitate, and may be recognized by its odor. What is the principal use of iodoform?

..  
..

## B. ALDEHYDES

(a) To 1 ml. of ethyl alcohol (95 per cent) add a few drops of concentrated sulfuric acid and 1 ml. of the oxidizing agent, potassium dichromate solution. Warm gently to boiling and note the

sharp, penetrating odor of the escaping gas acetaldehyde. This is also a test for ethyl alcohol.

(b) Pour 2 ml of methyl alcohol in a test tube which is standing in a beaker of water. Heat a copper spiral wire (Fig. 28) to a red heat in the upper part of the laboratory flame. On withdrawing the copper observe the black deposit of copper oxide. Immediately lower it into the test tube of methyl alcohol. Repeat if necessary until the pungent vapor of formaldehyde is evident. Save the oxidized alcohol for the Hehner resorcin test.



Fig. 28—Copper Spiral for Oxidation of Methyl Alcohol



What is the oxidizing agent in the preceding action?

How are aldehydes formed from alcohols?

(c) REDUCING AGENT. Aldehydes are readily oxidized

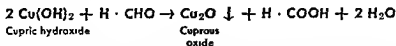
#### Instruction:

*When heating material in a test tube, always hold the test tube obliquely in the flame, point the mouth away from anybody and, if a liquid, slightly agitate it by a sidewise shaking of the test tube*

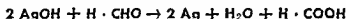
1. **Benedict's Cuprous Oxide Test:** Add a few drops of an aldehyde solution as formalin (40 per cent formaldehyde) (supply table) to 1 ml. of Benedict's solution, contained in a test tube. Make the solution more alkaline with a few drops of sodium hydroxide solution, and with constant agitation of the liquid boil gently for a



minute and then cool. A yellow to red insoluble  $\text{Cu}_2\text{O}$  is evidence of reduction.



2. *Tollen's Silver Mirror Test*: Clean a test tube by boiling with dilute sodium hydroxide solution. Add a few drops of an aldehyde as formaldehyde (supply table) to 1 ml. of Tollen's ammoniacal silver nitrate solution. Warm the tube very gently without agitating the liquid. Silver is deposited.



The results of 1 and 2 show that aldehydes are agents. In these reactions the metallic hydroxides furnish oxygen for the oxidation of the aldehyde (or ketone) to form organic acids.



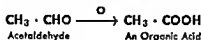
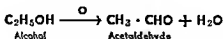
3. *Hehner's Resorcin Test*: Add one drop of a 1 per cent resorcin solution to the oxidized alcohol, obtained in (b). Add 5 ml. of water and mix well. Carefully pour this mixture down the side of a test tube containing about 3 ml. of concentrated  $\text{H}_2\text{SO}_4$ . A pink to a red ring (not brown) will be formed where the liquids meet. This is a method used to detect formaldehyde and thereby wood alcohol in a liquid.

Check tests 1, 2, 3 with the Instructor.

(d) *MILK TEST*: This test will detect one part of  $\text{H} \cdot \text{CHO}$  in 250,000 parts of milk. Add one drop of formalin to half a test tube of water. Mix thoroughly, pour out the solution, half fill the tube with milk, and shake so the milk will mix with the formalin clinging to the inside of the test tube. Add about 10 ml. of dilute  $\text{HCl}$  (one to three) and one drop of  $\text{FeCl}_3$  (5 per cent). After mixing thoroughly stand in a beaker and heat to boiling. Why might milk be found to contain formaldehyde?

### C. ORGANIC ACIDS

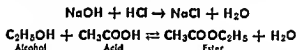
(a) To the undistilled liquid from the alcohol experiment add blue litmus paper.



What acid is formed?                      acid. Organic acids formed from alcohols are due to what kind of reaction?

#### D. ESTERS

(a) To a solution of 2 ml. of ethyl alcohol in a *dry* test tube add 1 cc. of glacial acetic acid and very carefully a few drops of concentrated sulfuric acid. Carefully warm (*very gently*). Add water, agitate the liquid and then notice the ethereal, fruitlike odor of ethyl acetate, an ester produced by the process *esterification*. Esters are extensively used as artificial flavors. Notice the similarity between this method of preparation and the method used to prepare a salt by neutralization. The alcohol acts like a base but is too weak to affect litmus. The similarity between neutralization and esterification is shown as follows:



(b) Repeat (a), using the same quantities of amyl alcohol, glacial acetic acid and concentrated sulfuric acid in a *dry* test tube. Warm *gently*. The odor is that of a finger nail polish remover, and resembles what fruit?

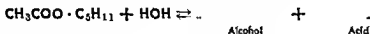
(c) Repeat (a), using the same quantities of the prepared (stock) methyl alcohol (wood)—salicylic acid solution and sulfuric acid in a *dry* test tube. Warm *gently*. What substance often used in liniments has this odor?

(d) Repeat (a), using the same proportions of ethyl alcohol, butyric acid, and sulfuric acid in a *dry* test tube. Warm *gently*. What tropical fruit has a similar odor?

(e) *Hydrolysis*: Esters are mostly insoluble in water and all undergo slight hydrolysis, *i. e.*, they react with water to form the

original acid and base. The hydrolysis of esters is just the opposite of esterification. The concentrated sulfuric acid used in the preparation of the ester is a dehydrating agent and absorbs the water as fast as formed and consequently prevents a reversible reaction. Put one-half a milliliter of amyl acetate (an ester) into a *dry* test tube and test with blue litmus paper. Add 10 ml. of  $H_2O$ . Shake the test tube thoroughly, remove the litmus paper, and compare the color with another piece of blue litmus paper. Result?

Write the formula of the alcohol and the acid formed in such a way as to show the characteristic group of each



What is the name of the alcohol formed?

### E. ETHER

To about 2 ml. of ethyl alcohol in a dry test tube, add drop by drop 0.5 ml. (eight drops) of concentrated sulfuric acid, shaking and smelling after the addition of each drop of acid. The odor is that of ordinary ethyl ether.



In the above reaction, what kind of an agent is sulfuric acid?

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What is the main use of ethyl ether?

## EXERCISE 29—CHAPTER XV

### CARBOHYDRATES

Section	Date	Name	..	...
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**MATERIALS** Starch, cane sugar, milk sugar, grape sugar, iodine solution, Benedict's solution, fermentation tubes, cooked starch paste (1 per cent), uncooled starch solution (1 per cent) Optional Phenylhydrazine solution, saturated sodium chloride solution, glucose solution, glacial acetic acid, microscope and slides

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#### Instructor:

*If D is to be performed start a day or so before the regular laboratory period.*

#### A. DEXTRIN FROM STARCH

(a) **IODINE TEST FOR STARCH:** Add a few grains of starch to 10 ml. of water. Heat to boiling, cool, and then add a drop of iodine solution. A blue color indicates the presence of starch. Reserve this test.

(b) **STARCH TO DEXTRIN:** Heat 3 Gm. of starch (5 ml.) in an evaporating dish on a wire screen over a very small flame with constant stirring. The flame must not touch the evaporating dish, and care must be taken not to burn the starch.\* At the end of several minutes the starch will become light brown. Continue the heating a few minutes longer with constant stirring. Cool. Use your finger to wipe up any unchanged starch clinging around the inside of edge of the dish. Fill the evaporating dish two-thirds full of water, stir, and filter. (While filtering, proceed to B.) Add a drop of iodine solution to 10 ml. of the filtrate. A violet to a reddish-brown color (not blue) indicates the presence of dextrin. To determine if the preparation of dextrin is successful, dissolve a pinch of dextrin from the supply shelf in a test tube half full of water, and make the test with iodine. Compare these solutions with the one saved in (a), and check results with the Instructor.

Evaporate the remaining filtrate to about

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\* If using the test tube holder to steady the evaporating dish while stirring, grasp the dish so as to enclose its lip

5 ml. and then with extreme caution *nearly* to dryness. Cool and taste a small portion of it. Why are toast and the crust of bread sweet? .... Examine the dextrin between

moistened fingers. Result?

What could it be used for?

### B. REDUCING PROPERTIES

To 5 ml. of water in a test tube add a few milliliters of grape sugar solution. Now add to this sugar solution just enough of Benedict's solution to make it a light blue color. Heat to the boiling point. The formation of yellow cuprous hydroxide or red cuprous oxide indicates that glucose is a reducing sugar. Test in a similar way dilute solutions of lactose, sucrose, and starch (cooked or uncooked).

Are monosaccharides (dextrose) reducing agents? The one

disaccharide which is not a reducing agent is Ara poly-

saccharides (starch) reducing agents? The reducing

power of carbohydrates is due to the characteristic group, called the

### C. HYDROLYZING PROPERTIES

(a) STARCH TO GLUCOSE: Boil 100 ml. of water in a beaker. Mix thoroughly by agitation in a test tube about one-half a gram of starch and 5 ml. of cold water. Add this mixture to the boiling water and stir. Add about 0.5 ml. of concentrated hydrochloric acid and boil gently for about five minutes. The solution should now be colorless. Drop a piece of litmus paper in the solution and add sodium hydroxide solution, a few drops at a time, until the solution upon stirring reacts neutral or slightly alkaline. Add sufficient Benedict's solution to give a blue color, and boil to make the test for glucose. Allow the solution to cool. Result?

Check with the Instructor

..... Complete the equation for the hydrolysis of starch (polysaccharides).

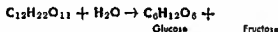


Hydrolysis of starch is produced in the mouth by \_\_\_\_\_ and  
in the intestines by \_\_\_\_\_

(b) SUCROSE INTO GLUCOSE AND FRUCTOSE. To 5 ml. of dilute cane sugar solution add a drop of hydrochloric acid and boil gently for two minutes. Make it alkaline to litmus paper with sodium hydroxide\* solution and test by Benedict's method. Result?

Check result with the Instructor

Complete the equation for the hydrolysis of cane sugar (disaccharide).



The fact that a starch solution is cloudy (colloidal) and a sugar solution is clear shows what about the relative sizes of the starch and sugar molecules?

What kind of an agent is hydrochloric acid?

Hydrolysis of sucrose is produced in the intestines by \_\_\_\_\_

In cooking fruits containing acid why should the sugar not be added until after the fruit is cooked?

Hydrolysis involves a reaction between a compound and \_\_\_\_\_

\* In the presence of a too strong solution of NaOH, a brown caramel like condensation product develops. The action of an alkali on a carbohydrate bearing a free carbonyl group to produce a brown product is noticed when too much soda is used as a leavening agent in baking.

**D. FERMENTATIVE PROPERTIES**

*(Demonstration by designated students)*

Fill five fermentation tubes (Fig. 29) with dilute solutions of starch, glucose, sucrose, lactose, and maltose, respectively. Introduce a few drops of yeast solution into each tube and place in a warm place until the next class

What carbohydrates do not ferment?

Under certain pathological conditions the urine may contain milk sugar. How could you determine whether the patient had diabetes or not, since milk sugar as well as dextrose responds to Benedict's test?



Fig 29

How do you account for the action of yeast on sucrose?

**E. OXIDATION**

Will a carbohydrate burn? In Exercise 26 a sugar was oxidized by copper oxide. What are the two compounds formed by oxidizing a carbohydrate? and What else is formed that cannot be shown in the equation for the oxidation of a sugar?

**Summary:**

*List four main chemical properties of carbohydrates*

The test for a monosaccharide and all disaccharides, excepting sucrose, is made by .

**F. DIGESTION OF STARCH PASTE**

*(Optional if Experiment on Digestion of Foods is to be performed)*

(a) **SALIVARY AMYLASE ACTION:** To 5 ml. of dilute cooked starch paste (1 per cent) in a test tube add five drops of saliva and stir thoroughly. Hold the bottom of the test tube in your hand so as to keep the liquid near body temperature. At half-minute intervals or less remove one drop to an evaporating dish (or depressions in a white porcelain test tablet), and test for starch with a drop of dilute iodine solution. When no color is produced with iodine, test the remaining mixture for sugar (maltose) by boiling with Benedict's solution, and cooling. What range of colors did you obtain?

What intermediate product is produced in the digestion of starch to sugar by salivary amylase (ptyalin)?

(b) Using 5 ml. of raw (uncooked) starch paste (1 per cent) add five drops of saliva, and mix thoroughly. Make the iodine test at one-minute intervals over ten minutes. Then filter and test the filtrate by Benedict's test. Result?

What is your conclusion?

.. .. .  
 .. . . .

**G. FORMATION OF OSAZONE (OPTIONAL)**

The monosaccharides and disaccharides, sucrose excepted, react with phenylhydrazine to form osazones. Since different osazones have slightly different crystalline forms with different melting points the formation of osazones identifies the sugar from which it was formed.

To a test tube containing a mixture of five drops of phenylhydrazine, ten drops of glacial acetic acid, and 15 drops of saturated sodium chloride solution, add 3 ml. of glucose solution and boil for about three minutes. Place the test tube in a beaker of boiling water, and allow to cool. Remove some of the crystals, place on a glass slide, examine under a microscope, and sketch one or more crystals.



## EXERCISE 30—CHAPTER XVI

### FAT—SOAP

Section	Date	Name
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**MATERIALS** Cottonseed oil, alcohol, sodium hydroxide (50 per cent), sodium chloride solution, sodium carbonate, potassium hydrogen sulfate, chloroform, ether, carbon tetrachloride, albumin solution, soap solution (1 10), 0.5 per cent sodium carbonate solution, rancid oil (one drop oleic acid to 2 cc of cottonseed oil), fresh olive oil, milk, blue litmus solution, pancreatic juice (0.1 Gm pancreatin in 500 ml of 0.5 per cent  $\text{Na}_2\text{CO}_3$ ), butter, glycerol, 2 per cent iodine-chloroform solution

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#### A. FAT

(a) **DIGESTION OF FAT:** Add sufficient blue litmus solution to 10 ml. of fresh milk to impart a noticeable blue color. Divide equally into two test tubes, and to the one add 1 ml. of artificial pancreatic juice. If both tubes are not the same color, add enough 0.5 per cent  $\text{Na}_2\text{CO}_3$  solution to the one needing more alkali. Allow both tubes to stand in a beaker of warm water, approximately  $37^\circ\text{C}$ ., until near the end of the laboratory period or longer. If an incubator is available, place the tubes in it instead of in the beaker of water. Hold the tubes together and compare their color by looking down into both tubes. The color of the litmus solution which contains pancreatic juice is \_\_\_\_\_, which indicates that an

\_\_\_\_\_ is formed. In case the change in color is not very marked, warm slightly and smell both tubes. What is the odor of the milk containing the pancreatic juice? \_\_\_\_\_ What enzyme found in the pancreatic juice digests fat?

**N. B** If the experiment on the Digestion of Foods (pp. 735 to 738) is to be performed, the following paragraph may be omitted.

Put a very small piece of butter into a test tube, add 5 ml. of water and warm until the butter barely melts. Add 5 ml. of pancreatic juice and shake thoroughly. Place the tube in the beaker of warm water and at the end of the laboratory period note the change in odor. What acid has been formed? \_\_\_\_\_ .  
Note the change in appearance of the butter.

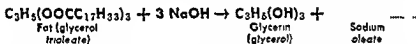


minutes or more. Again shake the tube. Result? . . . . .  
Structurally how does an unsaturated fat, such as olein, differ from  
a saturated fat?

Is the reaction of an unsaturated fat with iodine an example of addition or substitution?

### B. SOAP

(a) **SAPONIFICATION OF FATS.** Place in an evaporating dish 8 ml. of cottonseed oil, and an equal volume of ethyl alcohol (solvent) and 15 drops of the sodium hydroxide solution (50 per cent) from the supply table. Stir, and with a small flame warm *very gently* until the alcohol evaporates. (If the alcohol catches fire no harm is done, but extinguish by placing a sheet of paper on top of the dish.) The pasty mass, mainly sodium oleate mixed with glycerin, is soap. The process of treating a fat with an alkali to form a soap is called



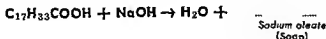
(The alcohol is used as solvent to save time and is not used commercially.)

(b) **FATTY ACIDS.** To the soap in the evaporating dish add water and warm to dissolve the soap. Save one-half a test tube of this solution for the next experiment, and to the remaining soap solution add a strong mineral acid as hydrochloric acid until a precipitate (liquid here) forms upon stirring vigorously.



Heat the mixture to boiling and filter through a wet filter. The residue on the filter paper is oleic acid and the above reaction represents a general method of obtaining an organic acid from its salt.

Is it soluble in water? Transfer some of the liquid or the solid residue from the filter paper to a test tube, add 10 ml. of water and a few milliliters of sodium hydroxide solution. Heat until solution takes place.



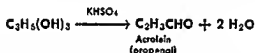
What characteristic property of an acid is shown in the above equation?

A soap is a metallic salt of a

(c) "SALTING OUT": To the one-half test tube of soap solution obtained in (b) add sodium chloride solution Result?

This is called "salting out," and is an example of precipitating a colloid What important commercial product is present in the brine below the soap?

(d) GLYCERIN (GLYCEROL): To a drop of glycerin in the bottom of a *dry* test tube add a few crystals of potassium hydrogen sulfate. Heat cautiously, and note the irritating odor of acrolein, which is formed by dehydrating glycerin according to the following equation:



Repeat the test for glycerin by using a few drops of any fat Why may this procedure be used as a test for any fat?

Since fats decompose when heated alone to a high temperature, would *intense* heat used in cooking fatty foods improve their flavor and digestibility?

## EXERCISE 31—CHAPTER XVII

### PROTEINS

Section	Date	Name
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**MATERIALS:** *Egg albumin solution (white of one egg thoroughly shaken with 300 ml of water), 1 per cent  $\text{CuSO}_4$  solution, Millon's reagent (one part by weight of mercury dissolved in two parts by weight of concentrated nitric acid and diluting the resulting solution with two volumes of water), dilute solutions of phenol, gelatin, mercuric chloride, lead acetate, silver nitrate, copper sulfate, ferric chloride, tannic acid (fresh), picric acid, dilute acetic acid, alcohol, ammonium sulfate crystals Cotton thread, silk thread, wool yarn*

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#### A. SOLUBILITY

(a) Obtain approximately 150 ml. of egg white solution from the supply table. Observe the flaky precipitate. What simple protein is not soluble in plain water, but is soluble in salt water? Start the filtering of the entire quantity of egg white solution, and use the clear egg albumin solution for the following protein reactions:

(b) What kind of a solution does albumin form with water?

Can albumin (colloidal) be separated from solution by filtering through filter paper? It can be separated unaltered though from a crystalloid in solution by a process called

(c) Place a few milliliters of albumin solution in a test tube and shake vigorously. What is characteristic of protein solutions upon shaking?

Can colloidal food be absorbed directly by the intestinal wall? What changes the colloidal material into an easily absorbable form?

#### B. COLOR REACTIONS

##### Instruction:

*Color reactions are due to a reaction between some one or more of the radicals of the complex protein molecule and the chemical reagent used in any test.*

(a) **XANTHOPROTEIC REACTION:** To about 3 ml of egg albumin solution in a test tube add a few drops of concentrated nitric acid. A white precipitate forms, which upon heating turns yellow and finally dissolves, imparting to the solution a yellow color. Cool and cautiously neutralize by adding the alkali, ammonium hydroxide, in excess. The yellow color deepens to an orange. Nitric acid on the skin produces a yellow color, which becomes orange when treated with ammonia water or soap.

(b) **BIURET TEST:** To 3 ml of egg albumin solution in a test tube add 1 ml. of sodium hydroxide solution and then slowly a few drops of a 1 per cent copper sulfate solution. At the end of a minute a pink to violet color is produced.

(c) **MILLON'S REACTION:** To 3 ml. of egg albumin solution in a test tube add a few drops of Millon's reagent. A white precipitate forms which upon heating slowly turns \_\_\_\_\_ and then \_\_\_\_\_. This color is due to the hydroxyphenyl group ( $-\text{C}_6\text{H}_4\text{OH}$ ), which is present in many proteins. Repeat Millon's test with a solution of phenol ( $\text{C}_6\text{H}_5\text{OH}$ ), and then of gelatin. Result and conclusions?

### C. COAGULATION OR HEAT TEST

(a) Pour a test tube full of dilute egg albumin solution into an evaporating dish, and heat to boiling. Complete coagulation may be obtained by acidifying with two drops of acetic acid. Remove some of the coagulated albumin and make the biuret test. Allow to stand for a minute. What is the color of the coagulation?

(b) Fill a test tube almost full of albumin solution. With a small flame carefully heat the middle portion of the liquid in the test tube to boiling by inclining the tube over the flame. Compare the lower part to the heated part. Result?

(c) Pour out half of the solution, heat the remaining portion to boiling, and filter. Make the biuret test on the filtrate. Result?

**What is the effect of heat on protein in solution?**

When heating milk or making soups from meat, what is the coagulated substance collected on the surface of the liquids?

(d) Place 5 ml. of clear albumin solution into three separate test tubes. To the first add one drop of dilute acetic acid, and to the second four drops of dilute sodium hydroxide. Place all three tubes in a beaker of water. Heat the water and watch to see what happens. Is coagulation facilitated by dilute acid or alkali? Add 2 ml. of concentrated hydrochloric acid to the acid tube and boil. Add 2 ml. of sodium hydroxide (10 per cent) to the alkali tube and boil. Results?

**D. PRECIPITATION REACTIONS**

Various salts, mineral acids, alkaloidal reagents, and alcohol are able to precipitate proteins.

(a) **PRECIPITATION BY SALTS OF HEAVY METALS** Prepare five test tubes, each containing about 3 ml. of dilute egg albumin solution and a drop of sodium hydroxide solution. To the first test tube add mercuric chloride solution, *drop by drop*, until an excess of the reagent has been added, noting any changes which may occur. Repeat, using lead acetate, silver nitrate, copper sulfate, and ferric chloride solutions.

<i>Salts of Heavy Metals</i>	<i>Results</i>
HgCl <sub>2</sub>	
Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	
AgNO <sub>3</sub>	
CuSO <sub>4</sub>	
FeCl <sub>3</sub>	

Egg albumin is used as an antidote for mercury or lead poisoning  
Why?

(b) **PRECIPITATION BY ALKALOIDAL REAGENTS** Prepare two test tubes, each containing 3 ml of dilute egg albumin solution and a drop of dilute acetic acid. To one add a few drops of tannic acid solution and to the other add a few drops of picric acid solution.

Results?

(c) **PRECIPITATION BY NITRIC ACID (HELLER'S RING TEST)** Place 5 ml of concentrated  $\text{HNO}_3$  in a test tube. Incline the tube, and by means of a pipette (glass tube) allow the dilute albumin solution to flow slowly down the side. A white zone of precipitated albumin forms at the point of juncture. This is a very delicate test and is used extensively in urinalysis.

(d) **PRECIPITATION BY ALCOHOL** Add a few drops of egg albumin solution to 5 ml of alcohol contained in a test tube. The fixing of tissues for histological examination by means of alcohol is an illustration of the application of this transformation produced by alcohol. The proteins are precipitated unaltered, and probably are dehydrated by the alcohol.

(e) **'SALTING OUT'** To a test tube one third full of egg albumin solution add ammonium sulfate crystals slowly and with constant stirring until a saturated solution is formed. The proteins are precipitated unaltered. Filter off the precipitate and test the filtrate for protein by any one of the previously tried tests. Is albumin completely precipitated in a saturated solution of ammonium sulfate?  
Check result with the Instructor.

In the previous precipitations the protein had combined with the reagent, D (a), (b), (c), or it had been coagulated by heat, C (a), or alcohol, B (d), so that it was permanently changed. In last week's experiment (Fats) what colloidal substance was 'salted out' of solution?



**Summary:**

Protein in solution may be precipitated by

**E. TEXTILE FIBERS**

*(Optional)*

Obtain from the supply table, nine threads, three each of wool, silk, and cotton for the following experiments.

(a) **EFFECT OF HEAT:** Light separately the end of a thread of wool, silk, human hair, and cotton; then withdraw from the flame

Which continues to burn?

Which gives the least odor?

How may you distinguish between animal fibers (wool, silk) and vegetable fibers (cotton, linen)?

(b) **EFFECT OF A STRONG BASE** Place a thread of wool, silk, and cotton in separate test tubes, each about one-eighth full of sodium hydroxide solution (10 per cent) and boil gently for a minute

Result?

What kind of fiber is dissolved?

What is the

composition of this kind of fiber?

(c) **EFFECT OF A CONCENTRATED STRONG ACID.** Repeat (b), using concentrated hydrochloric acid instead of the sodium hydroxide solution? Result?

(d) **EFFECT OF SALTS FROM THE BODY** How do the salts of the body in perspiration affect the protein fibers as in silk and wool?

(e) **SUMMARIZE THE PROPERTIES OF ANIMAL AND VEGETABLE FIBERS**

<i>Effect of</i>	<i>Animal Fiber</i> (wool and silk)	<i>Vegetable Fiber</i> (cotton)
Heat (flame)		
Bases (strong) (NaOH)		
Acid (conc ) (HCl)		

## EXERCISE 32—CHAPTER XVIII

### THE CHEMISTRY OF DIGESTION

Section	Date	Name
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**MATERIALS** Starch paste (one gram of starch ground thoroughly in a mortar with enough water to make a thin paste, and then poured slowly into 100 ml. of boiling water), dilute iodine solution, Benedict's solution, raw starch solution (1 per cent), artificial pancreatic juice (one gram pancreatin in 100 ml. of 0.5 per cent  $\text{Na}_2\text{CO}_3$ ), hard-boiled egg white, neutral pepsin (1 per cent), artificial gastric juice (1 Gm. pepsin in 100 ml. of 0.4 per cent  $\text{HCl}$ ), 0.5 per cent  $\text{Na}_2\text{CO}_3$  solution, cream, porcelain test tablets

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#### A. STARCH

(a) **SALIVARY AMYLASE:** Have ready about 3 ml. of dilute iodine solution for your different starch tests. To 5 ml. of cooked starch paste (1 per cent) in a test tube add five drops of saliva and stir thoroughly. At two-minute intervals or less, remove one drop to an evaporating dish (or depression in a white porcelain test tablet), and test for starch with a drop of dilute iodine solution. When no color is produced with iodine, test the remaining liquid for sugar (maltose) by boiling with Benedict's solution, and then cooling.

What range of colors did you obtain in the iodine tests?

What intermediate product is produced in the digestion of starch to sugar by salivary amylase (ptyalin)?

Using 5 ml. of raw (uncooked) starch paste add five drops of saliva, and mix thoroughly. Make the iodine test several times during the next 10 or 15 minutes. Filter, and test the filtrate for sugar by boiling with Benedict's solution.

What difference do you find in the digestive action and time action of saliva on cooked and uncooked starch?

#### B. FATS

(a) **PANCREATIC LIPASE (STEAP SIN):** To 1 ml. of cream add 5 ml. of milk or water, and an equal volume of artificial pancreatic juice.

Shake the mixture thoroughly. Keep at  $37^{\circ}\text{C}$  for an hour or more, and note any change in odor. Warming the tube will make the odor more noticeable. The smell indicates that the substance formed is an

Fats must be in an emulsified condition before they can be hydrolyzed. In the hydrolysis of fats what products are formed?

### C PROTEINS

(a) GASTRIC PROTEASE (PEPSIN) AND PANCREATIC PROTEASE (TRYPSIN). Place a small piece of the white of a hard boiled egg in three separate test tubes.

- 1 To the first add 10 ml of artificial gastric juice
- 2 To the second add 10 ml of artificial pancreatic juice
- 3 To the third add 10 ml of water as a control

Label the tubes and keep at  $37^{\circ}\text{C}$  for several hours. Examine at the end of several hours for indications of digestion.

What digests proteins?

Filter the liquids in which digestion appeared to take place and make the biuret test on each filtrate. Result?

Pancreatic juice contains three ferments

- 1 Trypsin, which changes albumin or proteins to peptones
- 2 Amylopsin, which changes starch to glucose
- 3 Steapsin, which emulsifies and hydrolyzes fats or oils

Why in all digestion experiments should the temperature of the test tube not vary widely from  $37^{\circ}\text{C}$ ?

### EXERCISE 33—CHAPTER XVIII

#### MEDIUM FOR ENZYME ACTION

Section	Date	Name
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**MATERIALS** *Starch, paste (1 per cent), 0.4 per cent HCl, 0.5 per cent  $\text{Na}_2\text{CO}_3$ , neutral pepsin solution (1 per cent), neutral pancreatin (1 per cent), hard boiled egg white, 1 per cent  $\text{CuSO}_4$ , dilute iodine solution*

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(a) **SALIVARY AMYLASE** Place 2 ml of starch paste (1 per cent) and five drops of saliva in each of three test tubes.

1. To test tube 1 add 2 ml. HCl (0.4 per cent).
2. To test tube 2 add 2 ml.  $\text{Na}_2\text{CO}_3$  (0.5 per cent).
3. To test tube 3 add 2 ml.  $\text{H}_2\text{O}$  (control tube).

Label, mix by agitating the contents of each tube, and keep at  $37^\circ\text{C}$ . in a beaker of water. Test a drop of each tube frequently with a drop of iodine until certain of the best medium for salivary digestion. Result?

**NOTE** The nine test tubes used in this and the next two tests may be conveniently placed in a beaker for incubation. If pressed for time, or for space in the incubator, a group of students, with the consent of the instructor, may work together.

(b) **PEPSIN:** Place uniform sized pieces of the white of hard-boiled egg and 2 ml of neutral pepsin solution (1 per cent) in each of the three test tubes.

1. To test tube 1 add 2 ml. HCl (0.4 per cent).
2. To test tube 2 add 2 ml.  $\text{Na}_2\text{CO}_3$  (0.5 per cent).
3. To test tube 3 add 2 ml.  $\text{H}_2\text{O}$  (control tube).

Keep at  $37^\circ\text{C}$ . for several hours. Compare the appearance of the tubes, and then make the biuret test in each tube. What is the best medium for pepsin digestion of protein?

(c) **PANCREATIC PROTEOLYSIS.** Place a uniform sized particle of the white of a hard-boiled egg in 2 ml of neutral pancreatin (1 per cent) in each of three test tubes

4. To test tube 4 add 2 ml. HCl (0.4 per cent).
5. To test tube 5 add 2 ml.  $\text{Na}_2\text{CO}_3$  (0.5 per cent).
6. To test tube 6 add 2 ml.  $\text{H}_2\text{O}$  (control tube).

Label and keep at 37° C and examine at the end of one hour. Compare and make the biuret test in each tube. Results and conclusions?

(d) PANCREATIC AMYLOLYSIS Place 2 ml of starch paste (1 per cent) and 2 ml of neutral pancreatin (1 per cent) in each of three test tubes

7 To test tube 7 add 2 ml HCl (0.4 per cent)

8 To test tube 8 add 2 ml  $\text{Na}_2\text{CO}_3$  (0.5 per cent)

9 To test tube 9 add 2 ml  $\text{H}_2\text{O}$  (control tube)

Label and keep at 37° C for one hour. Follow the digestion with the iodine test. What is the most favorable condition for the action of amylopsin?

What are your conclusions regarding the optimum reaction of the following enzymes

*Ptyalin*

*Pepsin*

*Trypsin* (pancreatic protease)

*Amylopsin* (pancreatic amylase)

## EXERCISE 34—CHAPTER XVIII

### TESTS FOR NUTRIENTS IN FOODS

Section	Date	Name
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**MATERIALS** *Iodine solution, Benedict's solution, 1 per cent copper sulfate solution, grape sugar solution, ether, starch, flour, potatoes, butter, green and ripe bananas, carrots, onions, cheese, peanut butter, cooked egg white, cooked egg yolk, other foods as time permits*

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(a) **STARCH:** Boil a few grains (not grams) of starch in a test tube half full of water. Cool by holding it under running cold water, and then add one drop of iodine solution. A deep blue color indicates starch. Test in a similar way the food samples. The egg should be hard boiled before testing.

(b) **GLUCOSE:** Add a few drops of grape sugar solution to half a test tube of water, and then Benedict's solution sufficient to give a very light blue. Boil. A yellow to red precipitate indicates the presence of a simple sugar such as glucose or fructose. What disaccharides show reducing properties?

Test the food samples for sugar by boiling small pieces of each in water colored blue with Benedict's solution.

(c) **FATS:** Meats and butter furnish most of the fats which serve as food. To examine foods for oil or fat, shake carefully a small portion of the food with half a test tube of ether. Filter into an evaporating dish and allow the filtrate to evaporate without heating. The residue in the dish when placed on paper, warmed and held to the light will be translucent as an indication of a fat

(d) **PROTEINS** Pour a few milliliters of the biuret reagent, prepared by adding a drop of a 1 per cent  $\text{CuSO}_4$  solution to a few milliliters of  $\text{NaOH}$  solution, upon a small portion of the food sample. Allow to stand for a few minutes. A pink to violet indicates protein.

(e) **MINERAL MATTER:** Burn a very small sample of food such as cheese on an evaporating dish until all of the black carbon is oxidized. What is the residue?

. .

Analyze the different foods on the supply table for starch, glucose, protein, and fat, and indicate by a positive sign (+) the nutrients found in each food.

**Analysis of Foods**

<i>Food</i>	<i>Starch</i>	<i>Glucose</i>	<i>Protein</i>	<i>Fat</i>
Banana, ripe				
Banana, green				
Butter				
Carrot				
Egg white (cooked)				
Egg yolk (cooked)				
Flour				
Onion				
Peanut Butter				
Potato				
Cheese				



**EXERCISE 35—CHAPTER XIX****TESTS FOR SOME BLOOD CONSTITUENTS**

Section	Date	Name
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**MATERIALS** Blood lancet, 0.85 per cent NaCl solution, 10 per cent sodium tungstate solution,  $2/3 N \cdot H_2SO_4$  (35 Gm conc. C. P.  $H_2SO_4$  diluted to a volume of one liter), Folin-Wu blood sugar reagent (dissolve in 100 ml of  $H_2O$  10 Gm anhydrous sodium carbonate, 1.88 Gm tartaric acid, 1.125 Gm  $CuSO_4 \cdot 5 H_2O$ , and dilute to 250 ml),  $AgNO_3$  solution,  $H_2O_2$  solution, freshly prepared saturated solution of benzidine in glacial acetic acid, glass slides, cover glasses, microscope, 1 ml of fresh (oxalated) blood for each student, cork to fit test tube

**Blood** It may be possible to obtain suitable oxalated or citrated blood and also blood plasma from a hospital. Where only a few drops of blood are needed it is best provided by the student by pricking the tip of a finger with a sterile needle, etc. Usually beef blood can be obtained from a slaughter house (abattoir). Place in a flask 0.2 gm of powdered potassium oxalate for each 100 ml of blood. Immediately upon obtaining the blood from the animal pour it into the flask, stopper securely, and gently swirl the flask to dissolve the oxalate. Also, any veterinarian should be able to obtain a pint or more of blood from the jugular vein of a cow without any injury to the animal.

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(a) **MICROSCOPIC APPEARANCE:** Place one drop of your own blood on a glass slide, cover with a cover glass, and examine under the microscope. Dilute the drop of blood (or a fresh drop of blood) with a few drops of isotonic sodium chloride solution, and again examine under the microscope. Draw some of the observed cells.

(b) **BLOOD PROTEIN PRECIPITATION.** Place 1 ml. (15 drops) of fresh blood (or oxalated blood) in a test tube, dilute with 7 ml. of water, and mix. Add 1 ml of 10 per cent sodium tungstate solution

and 1 ml. of sulfuric acid that is labeled  $2/3 \text{ N} \cdot \text{H}_2\text{SO}_4$ . Close the mouth of the tube with a cork and shake the tube vigorously. At the end of about five minutes a bright red to dark brown coagulum of the proteins forms. The sodium tungstate-sulfuric acid mixture forms tungstic acid, which, like tannic and picric acid, acts as an alkaloidal reagent.

What are alkaloidal reagents used for?

Filter through a wet filter paper into a test tube and save the protein-free filtrate for the next two experiments. If the filtrate is not clear, refilter through the same filter paper.

(c) **BLOOD SUGAR TEST.** To 2 ml. of the tungstic acid filtrate saved from (b) add an equal volume of the Folin-Wu blood sugar reagent (a modified Fehling's solution). Stand the tube for six minutes in a beaker of boiling water. Cool in running water (without shaking) for two or three minutes. A greenish-yellow to a yellowish-red color indicates that blood sugar has reduced the alkaline copper solution to cuprous oxide.

(d) **BLOOD CHLORIDE TEST.** To 2 ml. more of the tungstic acid filtrate from the Blood Protein Precipitation Test, add a few drops of nitric acid (filter if cloudy), and then some silver nitrate solution. Result?

..

What ion is silver nitrate a test for?

..

(e) **TESTING FOR CATALYTIC ACTION OF BLOOD.** If not familiar with the foaming produced by hydrogen peroxide on a bleeding cut, place a few drops of blood on a glass plate and add twice its volume of hydrogen peroxide. What causes the foaming?

(f) **BLOOD TESTS:** Of the several tests for the presence of blood, the benzidine test is the most delicate (1:5,000,000) and valuable for clinical work, while the hemin test is the most conclusive for medicolegal work

1. *Benzidine Test.* Dilute one drop of blood with a test tube of water. To 2 ml. of a freshly prepared saturated solution of benzidine

in glacial acetic acid, add an equal volume of hydrogen peroxide solution. Mix well, and add a few drops of the dilute blood solution.

**Result?** The intensity of the color depends upon the amount of blood present.

If a blood stain were on cloth would you use hot or cold water for removing the blood? Why?

2 *Hemin Test:* Place a very small drop of blood on a glass slide, dilute with a drop of water, add a minute crystal of sodium chloride, and carefully evaporate to dryness over a small flame. Adjust a cover glass, run underneath the glass a drop of glacial acetic acid, and warm gently until gas bubbles are noted. Add one more drop of acetic acid, allow to cool, and examine under the microscope for crystals of hemin (Teichmann's). Sketch some observed crystals

## EXERCISE 36—CHAPTER XIX

### CLOTTING AND PROPERTIES OF BLOOD

Section	Date	Name
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**MATERIALS** Test tube containing 5 ml of 24 hour old blood specimen from which the serum has separated test tube containing 5 ml of 24 hour old blood sample mixed with 0.01 Gm of powdered potassium oxalate (0.2 per cent solution of the oxalate in blood) 1 ml of fibrinated blood for each student ether or chloroform glass slides cover glasses microscope concentrated ammonium sulfide solution marble chips ( $\text{CaCO}_3$ ) cork to fit test tube 20% potassium oxalate needle or lancet two applicators or tooth picks skin disinfectant anti A serum and anti B serum

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#### A CLOTTING OF BLOOD

(*Demonstration and Reference to Text*)

(a) **BLOOD CLOT AND SERUM** Observe a test tube that contains 5 ml of a 24 hour blood specimen

What name is given to the light yellow liquid that has separated from the blood clot?

What is the name of the enzyme that causes blood to clot?

Why is the clotting of blood important?

Of what is the blood clot composed?

(b) **BLOOD ANTI COAGULANTS** Observe a test tube that contains 0.01 Gm of powdered potassium oxalate dissolved in 5 ml of a 24 hour old blood specimen What did the oxalate do to the calcium ions of the blood?

(*Demonstration*) Carefully add a few drops of a 1 per cent solution of calcium chloride to the oxalated blood and allow it to stand There should be an excess of calcium ions present but any great excess will hinder the clotting Does a clot form?

What metallic ion is necessary for the clotting of blood?

The normal clotting of the blood is hastened by the action of thromboplastin of the tissues in the presence of calcium

Why does the blood not normally coagulate in the veins?

(c) PREPARATION OF DEFIBRINATED BLOOD (Demonstration or previously prepared): Defibrinated or "whipped" blood is obtained by rapidly stirring *freshly* drawn blood until the fibrin separates as a stringy mass upon the stirring instrument. One ml. of defibrinated blood is needed for each student. How does fibrin differ in composition from the blood clot?

## B. PROPERTIES OF HEMOGLOBIN

(a) HEMOLYSIS OR LAKING OF BLOOD: When the hemoglobin of the red corpuscles escapes into the surrounding fluid, "hemolysis" or the "laking" of blood has taken place. To show that hemolytic action can be produced arrange three test tubes as follows:

No. 1. 9 ml. of distilled water + 9 drops of defibrinated blood.

No. 2. 2 ml. of 0.85 per cent NaCl solution + 2 drops of defibrinated blood.

No. 3. 2 ml. of 0.85 per cent NaCl solution + mixture of two drops of defibrinated blood and two drops of ether or chloroform.

Unchanged corpuscles give a cloudy (colloidal) appearance, while transparent solutions show that hemolysis has taken place. Place a drop from No. 1 tube on a slide, adjust a cover glass, and examine under a microscope. Examine a drop from tubes No. 2 and No. 3 in the same way. Compare the observed objects with the normal erythrocytes and leukocytes (see pp. 444 and 446). In what tube do you observe unchanged corpuscles?

What causes hemolysis?

How may anesthetics affect the erythrocytes of some patients?

... ..

Sometimes the bile enters the blood stream and indicates a condition known as jaundice. What effect does the bile have upon the red cells?

What prevents hemolysis from taking place in the plasma?

(b) **OXYHEMOGLOBIN AND HEMOGLOBIN (SO CALLED REDUCED HEMOGLOBIN)** Divide equally, in three test tubes the 9 ml of hemoglobin solution saved in tube No 1. Cover the mouth of one tube with a cork and shake it vigorously with the air in the tube. The bright red color is due to oxyhemoglobin. Save this tube for comparison.

Set up the carbon dioxide generator (Fig 30), and pass  $\text{CO}_2$  for a few minutes through 3 ml of dilute hemoglobin solution contained in the second test tube. Cover with a cork the mouth of this tube containing the dark solution, and shake it thoroughly with the air contained in it. What color change takes place?

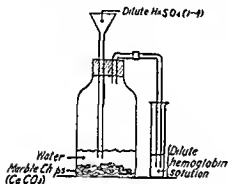


Fig 30— $\text{CO}_2$  Generator

In a few minutes the red color of the blood changes to a dark color owing to the  $\text{CO}_2$  driving out the oxygen and to some extent uniting with the hemoglobin.

Blood that is dark in color is poor in \_\_\_\_\_ but rich in \_\_\_\_\_

In what place in the body is reduced hemoglobin formed?

(Oxyhemoglobin may also be reduced by adding one drop of concentrated ammonium sulfide solution and gently warming the mixture.)

(c) **CARBON MONOXIDE HEMOGLOBIN** Pass natural gas (poisonous, contains some  $\text{CO}$ ) slowly through the third portion of dilute blood (hemoglobin) for at least ten minutes. Carbon monoxide hemoglobin is a trifle brighter tint (carmine) than oxyhemoglobin in strong solution. If there is no noticeable difference in color, dilute

this tube, and also the oxyhemoglobin tube saved from the previous experiment, with equal amounts of water. In very dilute solution the carbon monoxide hemoglobin assumes a bluish-red color, while the oxyhemoglobin appears yellowish-red. This test is frequently used in detecting carbon monoxide poisoning.

(d) **STABILITY OF CARBON MONOXIDE HEMOGLOBIN** (Demonstration): There are other agents besides CO that will reduce oxyhemoglobin, such as ammonium sulfide  $(\text{NH}_4)_2\text{S}$ . Add one drop of concentrated  $(\text{NH}_4)_2\text{S}$  to 5 ml. of dilute blood solution. Warm very gently, and note the change in color from red to dark, due to the formation of reduced hemoglobin.

Prepare 5 ml of carbon monoxide hemoglobin as in (c), add a drop of  $(\text{NH}_4)_2\text{S}$ , and note there is no change in color as in above. What does this show about the union of carbon monoxide with hemoglobin?

Explain how carbon monoxide poisoning gives rise to suffocation.

It is for a similar reason that the gases, hydrogen sulfide and nitric oxide, are poisonous

(e) **KALARMA'S TEST FOR CARBON MONOXIDE HEMOGLOBIN:** This test is not only easy to perform, but also will detect as little as 10 per cent of saturation with carbon monoxide.

Place about 10 ml. of water in each of two test tubes. To one test tube add five drops of the blood suspected of containing carbon monoxide, and to the other test tube add five drops of normal blood as a control solution. Add five drops of freshly prepared concentrated solution of ammonium sulfide to each test tube, mix gently, and then make faintly acid with acetic acid.

Blood containing carbon monoxide hemoglobin gives a rose to red color, the depth of color depending upon the concentration. The control solution containing the normal blood develops a dirty greenish brown color.

**C. BLOOD GROUPING\***

Label one slide *anti A* and another *anti B*.

Put a tiny droplet of potassium oxalate solution onto each slide.

After sterilizing both the finger tip (not index finger) and the needle or lancet, puncture the skin with a firm motion so as to cause blood to flow freely. (Suggestion: One student may puncture another student's finger). Add several drops of blood to the oxalate on each slide, mixing thoroughly with separate applicators or toothpicks, leaving ends of applicators in place on their respective slides.

Immediately add two drops anti A serum to the oxalated blood on the slide labeled *anti A* and two drops anti B serum to the slide labeled *anti B*, then mix well. Rock the slides gently for about one minute, then observe for agglutination.

Did anti A serum cause agglutination of your red blood cells?

Did anti B serum cause agglutination of your red blood cells?

I therefore conclude that my blood is Group  
(See page 453, 455 for interpretation.)

Check results with your Instructor.

\*Some workers use a concentrated solution of blood in physiologic saline solution for blood grouping.



## EXERCISE 37—CHAPTER XX

### NORMAL URINE

Section	Date	Name
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**MATERIALS** Six ounces of 24-hour sample of urine, Vogel scale, urinometer, centrifuge and tubes, microscope, slides and cover glasses, silver nitrate solution, barium chloride solution, acetic acid Magnesia mixture (dissolves 17.5 Gm of magnesium sulfate and 35 Gm of ammonium chloride in 140 ml of distilled water, add 70 Gm of conc.  $\text{NH}_4\text{OH}$ , and keep in a glass-stoppered bottle).

Beginning in the morning collect all your urine passed for the next 24 hours. After measuring, save six ounces for analysis

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#### A. PHYSICAL CHARACTERISTICS

(a) **VOLUME:** Using a liter graduate measure, record the volume of urine excreted                  ml High urine excretion is called while low excretion is called

(b) **COLOR:** Compare one-half a test tube of filtered urine with a Vogel scale and record the color                  How does the volume excreted affect the color of normal urine?

(c) **TRANSPARENCY.** Record the appearance (clear, turbid, etc.)

Turbid urine may be due to bacterial decomposition of urea, or to phosphates and urates, which will precipitate in a cold or low-acid urine. Permanent turbid urines are pathological. Phosphates dissolve on acidifying the urine with acetic acid, while urates become soluble upon warming the urine. Do you have phosphates or urates, or both, in your sample?

(d) **REACTION:** Record the action of litmus paper as neutral, faintly or distinctly acid, or alkaline

(e) **SPECIFIC GRAVITY:** Fill the urinometer cylinder three-quarters full with urine, remove any froth with a piece of filter

paper, introduce the urinometer slowly with a slight spin, allow it to come to rest free from the cylinder, and read the scale at the lowest part of the meniscus. Record the reading  
Normal urine varies from 1.015 to 1.024 at 25° C.

**INSTRUCTION:** *Rinse the urinometer with water, and return it and the cylinder to the instructor.*

(f) **TOTAL SOLIDS:** Multiply the second and third figures of the decimal portion of the specific gravity by 2.6 to get the approximate amount of solids in 1000 ml. Calculate the total solids in your 24-hour collection.

$$\frac{\text{(Decimal)} \times 2.6 \times \text{(24 hr volume)}}{\div 1000} = \text{(Total solids)}$$

Total solids usually vary from 40 to 60 Gm.

(g) **MICROSCOPIC EXAMINATION OF SEDIMENT (OPTIONAL):** Pour 15 ml of urine containing sediment into a centrifuge tube, and centrifuge at a moderate rate of speed for about three minutes. Drain off the liquid, transfer some of the sediment to a microscopic slide, add a drop of urine, cover with a cover glass, reduce the light to a minimum and examine under the low-power microscope.

Urinary sediments are classified as organized (formed elements) and unorganized (crystalline and amorphous) sediments, of which the organized are of the greatest clinical importance. To this latter group belong the *red corpuscles*, leukocytes, mucous threads, epithelium, spermatozoa, *cylindroids*, casts and pus. Examination of urinary sediment is frequently made with the primary object of determining the presence or absence of casts.

It is important that you become familiar with a normal urine before attempting a microscopic examination of pathological urine.

## B. TESTS FOR INORGANIC SALTS (OPTIONAL)

Before carrying out chemical tests, *filter* the urine until clear, and if albumin is present remove it by adding a few drops of nitric acid, boiling, cooling, and filtering.

(a) **CHLORIDES:** Acidify 10 ml. of urine with nitric acid, and add a drop of silver nitrate solution. Result? . . .

(b) *SULFATES*: Acidify 10 ml of urine with acetic acid, and add a drop of barium chloride solution. Result?

(c) *PHOSPHATES*. Make 10 ml of urine alkaline with ammonium hydroxide, and warm. Result?

The earthy phosphates or phosphates of calcium and magnesium separate. Filter off the earthy phosphates and add a small amount of magnesia mixture to the filtrate. Warm the solution. Result?

The alkaline phosphates or the phosphates of sodium and potassium separate. Which form of phosphates is present in the larger amount?

## EXERCISE 38—CHAPTER XX

### PATHOLOGICAL URINE

Section	Date	Name	
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**MATERIALS** Robert's reagent (five parts of saturated magnesium sulfate and one part of concentrated nitric acid), dilute acetic acid (3 per cent). Benedict's qualitative and quantitative solutions, test tubes (25 x 150 mm), 2 ml Mohr pipettes, sodium carbonate, sodium nitroprusside, 10 per cent ferric chloride, iodine solution (1 250 ml alcohol), freshly prepared saturated solution of benzidine in glacial acetic acid, Obermayer's solution (1 Gm. of  $\text{FeCl}_3$  in 500 ml.  $\text{HCl}$ ), hydrogen peroxide, chloroform. Collections of urine known to contain albumin, sugar, acetone bodies, bile, and blood

**NOTE:** In order to give a quantitative significance to a qualitative test, it is suggested that you use the terms "faint trace (delicate), trace, small, moderate, large," or "very large amount." It is also suggested that you carry out at the same time tests for both normal and pathological urines in order to see the contrasts between them, and thereby make your pathological tests more certain.

(a) **ALBUMIN:** The presence of albumin in the urine more frequently is associated with inflammatory or degenerative changes in the kidneys and less frequently with inflammatory changes in the tract below the kidneys. Tests for albumin in urines involve precipitation reactions, either due to the formation of an insoluble compound or the insolubility of the albumin in the reagent employed. Clear urines must be used in chemical tests. Clarify by filtering through filter paper, or, if necessary, by shaking with powdered magnesium oxide and then filtering.

**Coagulation Test:** Almost fill a test tube with urine, and heat the upper portion to boiling. If the heated portion becomes cloudy the turbidity may be due to phosphates. The addition of two drops of dilute acetic acid and warming again will dissolve the phosphates, while a more flocculent precipitate will be produced if only albumin is present.

**Heller's Test:** Place a few ml. of concentrated nitric acid in a test tube, slant the tube, and very carefully allow an equal amount of urine to slowly run down the side of the tube. The urine will float on the nitric acid, and a white ring (precipitated protein) will appear at the junction of the two liquids. Sometimes the white zone does not appear until allowed to stand for a few minutes.

**Roberts' Test** Using Roberts' reagent instead of nitric acid use the same procedure as in Heller's ring test. This test is more sensitive than the nitric acid test, but like Heller's test precipitates nucleoprotein and mucin. If a clear, white ring is not obtained at the contact zone, take another sample and run the "heat test." A cloudiness indicates albumin.

(b) **SUGAR** Small amounts (0.02 to 0.2 per cent) of reducing sugars may be present in normal urine, the nature of which is not understood. The presence of sugar in abnormally large amounts in the urine, called glycosuria, more frequently is the result of hyperglycemia (increased blood sugar), and less frequently the result of a low sugar threshold, called renal diabetes.

**Benedict's Test** To 5 ml of Benedict's qualitative solution in a test tube add not more than eight drops of urine, and, while agitating the tube, boil from one to two minutes. Allow to cool spontaneously. The formation of a green, olive green, yellow, or red precipitate indicates the amount of sugar present, the amount being designated as plus 1 ( $1\frac{1}{2}\%$  sugar), plus 2 ( $\frac{3}{4}\%$ ), plus 3 (1%), and plus 4 (2% or more) respectively. If the amount of dextrose sugar is under 0.3 per cent the precipitate forms on cooling.

**Myer's Quantitative Determination (Optional)** This determination is a modification of Benedict's method and is accurate enough for clinical purposes. Pipette\* 5 ml of Benedict's quantitative solution into a large test tube (25 x 150 mm), and then add 1 to 2 Gm of sodium carbonate. Using a folded piece of paper as a test tube holder held in the left hand, heat the solution to a vigorous boil, at the same time agitating the liquid. Using a 2 ml Mohr pipette held in the right hand, carefully run the urine into the boiling solution a drop at a time, until a white precipitate begins to form. Care must be taken at this point in adding the drops more slowly. The end point is reached when one drop clears up the last trace of blue color. Five ml of Benedict's solution will reduce 10 mg of glucose. The percent of glucose is found by dividing 1 by the number of ml's of urine used.

(c) **ACETONE BODIES** The presence of acetone bodies in the urine, called acetonuria or ketonuria, is the result of incomplete oxidation of fatty acids due to a failure to "burn" carbohydrates. Qualitative tests for acetone and acetoacetic acid are sufficient in

\* If unfamiliar with technique of using a pipette see Instructor

determining the existence of acidosis. The Rothberg test detects both acetone and acetoacetic acid (1 in 20,000), while Gerhardt's test detects only acetoacetic acid (1 in 8000).

*Rothberg's Test for Acetone and Acetoacetic Acid* Add a small crystal of sodium nitroprusside to 5 ml of urine, and shake until dissolved. Slant the tube, and by means of a glass tube or pipette carefully stratify (arrange in layer) about 2 ml of concentrated ammonium hydroxide upon the urine. At the end of five or ten minutes a violet zone will develop at the junction of the two liquids, if acetone is present. More than a trace of acetone is pathological.

*Gerhardt's Test for Acetoacetic Acid (Optional)* To 5 ml of urine in a test tube, add ferric chloride solution (10 per cent), drop by drop, until a precipitate forms. Filter and add a few more drops of ferric chloride solution. A deep red color indicates acetoacetic acid.

(d) **BILE** The presence of bile pigments in the urine is the result of obstruction to the flow of bile via the bile ducts into the intestine, and may be due to a calculus, catarrhal inflammation, or a growth of some kind. Considerable amounts of bile impart a dark yellow color to urine, the foam of which upon vigorous shaking has a distinct yellow color. Vigorously shake 5 ml of urine contained in a test tube.

*Gmelin's Test* Carefully superimpose 5 ml of urine upon an equal quantity of "yellow" nitric acid as in Heller's ring test for albumin. Upon standing for a few minutes and agitating very gently, a play of colors—green, blue, violet, red, and yellow will be seen in the presence of bilirubin.

*Iodine Test* Carefully superimpose dilute iodine (1:250) upon 5 ml of urine. A green ring indicates bile.

(e) **BLOOD** The presence of blood in the urine, called hematuria, indicates some lesion in either the kidney or in the urinary tract below the kidney. When in large amounts blood imparts a reddish cast to urine. The presence of blood is always pathological.

*Benzidine Test* To a test tube containing 3 ml of a saturated solution of benzidine in glacial acetic acid, add an equal volume of hydrogen peroxide (3 per cent), and a few drops of urine. A green to a deep blue color indicates the presence of blood.

(f) **INDICAN IN EXCESS:** The presence of indican in the urine indicates excessive putrefaction taking place in the intestine as the result of bacterial action.

*Obermayer's Test:* To one-fourth of a test tube of urine add an equal volume of Obermayer's solution. Add 2 ml. of chloroform and mix by shaking. Upon standing the indican is changed to indigo, which dissolves and imparts a more than faint blue color to the chloroform. There is sufficient indican in normal urine to give a faint blue color to the chloroform in the presence of Obermayer's reagent.

(g) **MICROSCOPIC STUDY (OPTIONAL):** If time permits, examine microscopically the sediment obtained from pathological urines.

## EXERCISE 39—CHAPTER XXI

### BASAL METABOLISM TEST

Section . Date Name ..

MATERIAL: *The Benedict Roth Metabolism Apparatus*

As a laboratory experiment it is suggested that the class be given an opportunity of witnessing a basal metabolism test, and to study some of the charts made.

NOTE: The following material is largely obtained from *Directions for Operating the Benedict-Roth Metabolism Apparatus*, furnished by Warren E. Collins, Inc.

#### A. PRELIMINARIES TO THE METABOLISM TEST

(a) **INSTRUCTIONS FOR THE INSTRUCTOR:** Several days in advance of the experiment select one student of the group of students as the subject of the test. Measure the height of the student in centimeters, and obtain the weight of student (without clothing) in kilograms.

(b) **INSTRUCTIONS FOR THE PATIENT:** On the evening before the test eat lightly, and retire early (by 10 P.M.) to get plenty of rest. Since digestion and absorption of food increase the rate of metabolism a basal metabolism can be determined only after about 14 hours of fasting.

On the morning of the test avoid bath, dress slowly, do with as little muscular movement as possible, don't eat any breakfast or drink any liquid except water, avoid smoking, get to the place of testing with as little exertion as possible, and recline at least 20 minutes before starting the experiment. The metabolism rate will be elevated unless there is complete muscular and mental repose previous to the testing.

#### B. EXPLANATION OF THE APPARATUS

The apparatus (Fig. 31) for measuring metabolism consists of a spirometer for holding pure oxygen with accompanying valves and tubes to allow rebreathing. The spirometer or oxygen bell is filled with oxygen, and the patient is connected to the metabolism tester by a mouthpiece. A nose clip is attached to the patient's nose and oxygen is inhaled from the spirometer through an intake valve (Fig. 32), and is exhaled through an expiratory valve back to the spirometer.



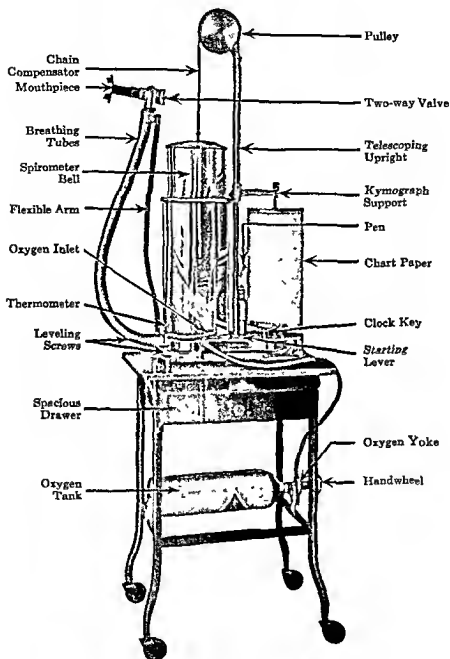


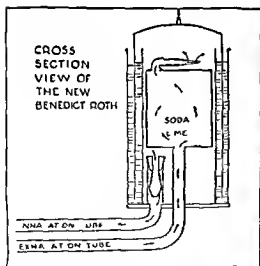
Fig. 31—Benedict-Roth Table, Oxygen Tank, and Principal Parts.



Fig 32—Mouthpiece—Nose Clip—Valve

In the passage back to the spirometer the expired gas passes through an inside container filled with soda lime ( $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ) which absorbs the  $\text{CO}_2$  exhaled by the patient (Fig 33) The fall of the spirometer indicates the oxygen consumed The gradual decrease in the volume of oxygen in the spirometer and the respirations are graphically recorded by a writing arm of the spirometer, which makes pen tracings over a chart

fastened to a revolving drum (Fig 34) The continuous series of upstrokes and downstrokes represent exhalations and inhalations respectively



DIRECTION OF RESPIRATIONS

Fig 33—Cross Section View Showing Direction of Respiration



Fig 34—Pen and Counterweight

### C. MAKING THE METABOLISM TEST

Prepare the apparatus by putting on a chart, sterilize a rubber mouthpiece and fill the pen with ink. Have the patient recline on a couch in a comfortable position. Apply the nose clip well down on the nostrils and adjust the thumbscrew firmly. Have the patient test the airtightness of the nose clip by attempting to exhale through the nose. Connect the mouthpiece and allow the patient to breathe room air through the slot in the free breathing valves for about one or two minutes. While allowing the patient to become accustomed to breathing through the mouthpiece fill the spirometer bell with oxygen, record the thermometer and the barometer reading. By means of the valve handle connect the patient to the breathing circuit of the machine. From now on, the spirometer will move up and down with each exhalation and inhalation, and the pen similarly. Set the clock in motion by moving its starting lever. Allow the test to run about eight minutes, and repeat after a few minutes' rest with a second period to check the first test. Remove the chart, select the best consecutive six-minute section of each record, draw a line through the bottom peaks (Fig. 35). The slope of this line indicates the rate of oxygen consumption (in terms of calories per hour) which is easily read from the six one-minute lines which it intersects. Where the time line selected as the beginning of the test crosses the slope line, take a reading. Count six-minute lines to the left and take a second reading. Subtract the smaller from the larger and the difference is the patient's actual oxygen consumption (Fig. 36)

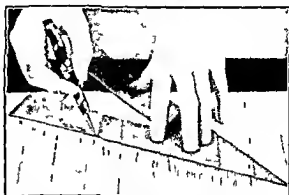
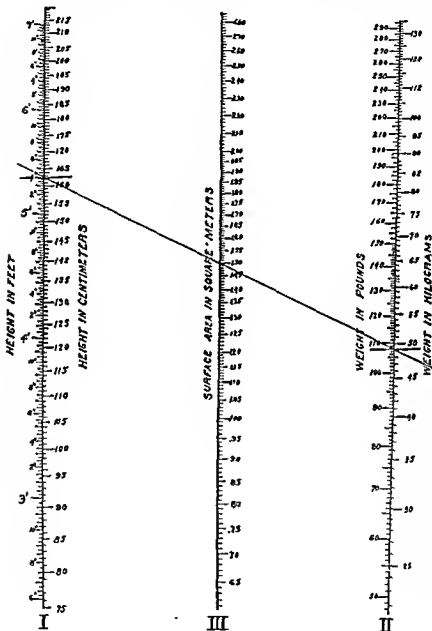


Fig 35—Drawing Slope Line.

### D. CALCULATIONS

(a) DETERMINATION OF NORMAL CONSUMPTION OF OXYGEN: Using a ruler, draw a line between the patient's height found in Column I and the weight in Column II. Read the Body Surface Area where the line intersects Column III. (This all refers to Table

TABLE A—DUBOIS BODY SURFACE CHART



(Prepared by Boothby and Sandiford of the Mayo Clinic.)

A) Transfer this body surface figure opposite "Column III" in the space for computations. Refer to Table B and using the patient's age (nearest birthday) and sex read the calories per square meter per hour (Table B). Transfer the figure beside "Table B"

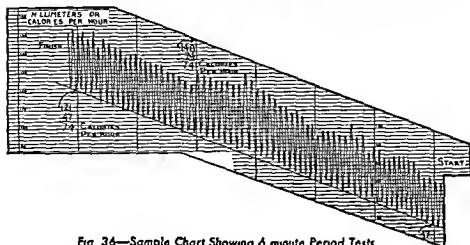


Fig 36—Sample Chart Showing 6 minute Period Tests

TABLE B—CALORIES PER SQUARE METER PER HOUR

Age	Males	Females	Age	Males	Females
5	(53.0)	(51.6)	20-24	41.0	36.9
6	52.7	50.7	25-29	40.3	38.6
7	52.0	49.3	30-34	39.8	36.2
8	51.2	48.1	35-39	39.2	35.8
9	50.4	46.9	40-44	38.3	35.3
10	49.5	45.8	45-49	37.8	<b>35.0</b>
11	48.6	44.6	50-54	37.2	34.5
12	47.8	43.4	55-59	36.6	34.1
13	47.1	42.0	60-64	36.0	33.8
14	46.2	41.0	65-69	35.3	33.4
15	45.3	39.6	70-74	(34.8)	(32.8)
16	44.7	38.5	75-79	(34.2)	(32.3)
17	43.7	37.4			
18	42.9	37.3			
19	42.1	37.2			

in space for computations. Multiply III  $\times$  B which will give the total Normal Calories Per Hour—the exact normal oxygen consumption for a person of this height, weight, age, and sex.

(b) DETERMINATION OF ACTUAL CONSUMPTION OF OXYGEN Transfer the difference in heights of the six minute test period to the space provided for it opposite  $O_2$  line Record the temperature of the spirometer and barometric pressure Using the Table C

TABLE C—CORRECTION FOR TEMPERATURE AND PRESSURE

Temperature in degrees Centigrade

mm	15	18	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
600	735	732	728	725	721	718	715	712	708	704	701	697	693	689	685	681	677	673	669	665	661
605	742	739	736	731	727	724	721	718	714	710	707	703	699	695	691	687	683	679	675	671	687
810	748	745	741	737	733	730	727	724	720	716	713	709	705	701	697	693	689	685	680	678	872
815	754	751	747	744	740	737	734	730	726	722	719	715	711	707	703	699	695	691	686	682	678
620	760	757	753	750	748	743	740	737	733	729	725	721	717	713	709	705	701	698	692	688	684
625	767	764	760	756	752	749	746	743	739	725	731	727	723	719	715	711	707	702	698	694	690
630	773	770	766	762	758	755	752	749	745	741	727	733	729	725	721	717	713	708	704	700	696
635	779	776	772	768	764	761	758	755	751	747	743	739	735	731	727	723	719	714	710	706	702
640	780	782	778	774	770	767	764	761	757	753	749	745	741	737	733	729	725	720	716	711	707
645	792	788	784	781	777	773	770	767	763	759	755	751	747	743	739	735	731	726	722	717	713
650	793	794	791	787	784	780	777	773	769	765	761	757	752	748	744	740	738	732	727	723	719
655	604	800	797	793	790	788	783	779	775	771	767	763	758	754	750	746	742	738	733	729	724
660	810	808	803	799	796	792	789	785	781	777	773	769	764	760	756	752	748	744	739	735	730
885	818	812	809	805	802	798	795	791	787	783	779	775	770	766	762	758	754	749	745	741	736
670	822	819	816	812	809	805	801	797	793	789	785	781	776	772	768	764	760	755	751	748	742
875	828	825	821	818	818	811	807	803	799	795	791	787	782	778	774	770	766	761	757	752	748
680	834	831	827	824	821	817	813	809	805	801	797	793	788	784	780	776	771	767	763	758	754
685	841	837	833	830	827	823	819	815	811	807	803	799	794	790	786	782	777	773	769	764	760
690	848	844	841	837	833	829	825	821	817	813	809	805	800	796	792	788	785	779	775	770	765
695	854	850	847	843	839	835	831	827	823	819	815	811	806	802	798	794	789	785	780	776	771
700	860	858	853	849	845	841	837	833	829	825	821	817	812	808	804	800	795	791	788	781	777
705	808	862	859	858	851	847	843	839	835	831	827	823	818	814	810	806	801	796	792	787	783
710	872	880	885	881	887	883	879	875	871	867	863	859	854	850	846	842	837	832	798	793	788
715	878	874	871	867	865	859	853	845	847	843	839	835	830	828	822	818	813	808	804	799	794
720	885	881	877	873	869	865	861	857	853	849	845	841	838	832	828	824	819	814	810	805	800
725	891	887	883	879	878	872	867	863	869	855	851	847	842	838	834	830	825	820	816	811	806
730	897	894	890	886	882	878	874	869	865	861	857	853	848	844	840	836	831	828	822	817	812
735	904	900	896	892	888	884	880	875	871	867	863	859	854	850	846	842	837	832	827	822	817
740	910	908	902	898	894	890	886	881	877	873	869	865	860	855	852	848	843	838	833	828	823
745	916	912	908	904	900	896	892	887	883	879	875	871	866	862	857	853	848	844	839	834	829
750	922	918	914	910	906	902	898	893	889	885	881	877	872	868	863	859	854	849	845	840	835
755	928	924	920	918	912	908	904	899	895	891	887	883	878	874	869	865	860	855	851	846	841
760	934	930	928	922	918	914	910	905	901	897	893	889	884	880	875	871	866	861	857	852	847
765	941	938	932	928	924	920	916	911	907	903	899	895	890	886	881	877	872	867	863	857	852
770	947	943	939	935	930	926	922	917	913	909	905	901	896	892	887	883	878	873	869	863	858
775	954	949	945	941	936	932	928	923	919	915	911	907	902	898	893	889	884	879	875	869	864
780	960	956	952	948	943	939	935	930	926	921	917	913	908	904	899	895	890	885	880	876	870

draw a circle around the temperature and the barometer readings and at the intersection of these two columns you will find the correction factor Transfer this figure opposite "Table C" in space provided for computations Multiply the difference in height for the six minute test period (from kymograph tracing) by O line by Table C which will give the total actual Test Calories Per Hour

(c) **DETERMINATION OF BASAL METABOLIC RATE:** To find the relation of the Normal Calories Per Hour to the Actual Test Calories Per Hour in terms of per cent subtract the smaller from the larger, and divide the difference by the normal, and multiply by 100. This is the Basal Metabolic Rate in per cent. If the Actual test is greater than the Normal the result is plus, and if less the result is minus

### DATA AND COMPUTATIONS

Sample		Patient	
Name	Date	Name	Date
Age 49 Yrs 4 Mo	Height 5' 4"	Age	Yrs Mo Height
Wt 108 lbs		Wt	
Temperature	Barometer	Temp	Bar Press
Normal	Actual Test	Normal	Actual Test
Column III = 1 50	O <sub>2</sub> line = 74	Column III =	O <sub>2</sub> line =
Table B = 35	Table C = 0 902	Table B =	Table C =
III × B = 52 5	O <sub>2</sub> × C = 66 748	III × B =	O <sub>2</sub> × C =
$\frac{66.75 - 52.5}{52.5} = + 27 \text{ B M R}$		B M R =	
Pulse	72-70	Pulse	
Body Temperature	98 0	Body Temperature	
Blood Pressure	110-80	Blood Pressure	

Does the calculated basal metabolism of the subject fall within 10 per cent of the theoretical? Suggest reasons why the percentage deviation of the basal metabolism as carried out is likely not to be a true record of the basal metabolism

### E. SPECIFIC DYNAMIC ACTION OF PROTEIN

As an interesting sequel to the determination of the basal metabolism the following experiment can be performed.

Feed the same pseudo-patient 250 Gm. of fried chopped meat, and at the end of one hour's rest repeat the metabolic determination.

<i>Data</i>	<i>Computation</i>
Temperature =	
Bar. Press. =	
O <sub>2</sub> line =	
Table C =	
O <sub>2</sub> × C =	
B.M.R. =	
Pulse =	
Body Temp. =	
Blood Press. =	

Is there any specific dynamic action produced by proteins?



### F. CONDITIONS AFFECTING METABOLIC RATE

The following list gives the most common conditions which influence the metabolism test and show an increased or decreased metabolic rate.

#### Increased Metabolic Rate in

- 1 Hyperthyroidism
- 2 Hyperpituitarism, Acromegaly, Gigantism
- 3 Leukemia Lymphatic and Myelogenous
- 4 Anemia, when severe
- 5 Malignancy, in about 30 per cent of cases
- 6 Hodgkin's Disease
- 7 Diabetes, when moderate
- 8 Acidosis, when severe
- 9 Arterial Hypertension
- 10 Fever 7 per cent increase for each °F of rise of body temperature (DuBois)
- 11 Convalescence from wasting diseases, and rapid growth

#### Decreased Metabolic Rate in

- 1 Post-Thyroidectomy
- 2 Myxedema
- 3 Cretinism
- 4 Thyrogenous Obesity
- 5 Hypopituitarism
- 6 Hypophyseal Obesity
- 7 Hypoadrenalism
- 8 Addison's Disease in about 15 per cent of cases
- 9 Undernutrition, Starvation
- 10 Epilepsy
11. Arterial Hypotension
- 12 Nephrosis

### G. SOME TYPES OF RESPIRATIONS

Determinations of the Metabolic Rate show the character of respirations. The following spiograms show types associated with some common disorders



Fig 37—Normol.



Fig 38—Toxic Goiter

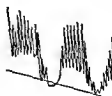


Fig 39—Cardiac Difficulty

## EXERCISE 40—CHAPTER XXIII

### MILK

Section	Date	Name
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**MATERIALS** *Hydrometer (lactometer or urinometer), whole and skimmed milk, copper sulfate solution (1 per cent), 10 per cent acetic acid, 95 per cent alcohol, ether, junket tablets, Benedict's solution, ammonium molybdate solution, sodium alcoholate (10 per cent alcoholic solution of sodium hydroxide), ammonium oxalate solution*

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#### A. GENERAL CONSIDERATIONS

1. **REACTION:** Test the reaction of fresh whole milk with red and blue litmus paper. Is it acid, basic or neutral?

2. **SPECIFIC GRAVITY:** The specific gravity of normal cow's milk should not be lower than 1.029 at 60° F., if legal. Using a hydrometer take the specific gravity of both whole and skimmed milk.

The sp. gr. of whole milk is \_\_\_\_\_, of skimmed milk is \_\_\_\_\_

The difference is due to \_\_\_\_\_

How could skimmed milk be cheaply changed so as to have the same sp. gr. as whole milk?

3. **FILM FORMATION:** Pour a test tube of whole milk into an evaporating dish and heat until a scum forms on top of the milk. Recalling the action of white of an egg in very hot or boiling water, what same nutrient in milk is shown by coagulation?

Remove some of the scum with a stirring rod and place in a test tube. Make the biuret test by adding 5 ml. of 10 per cent sodium hydroxide solution, and then carefully add a few drops of very dilute copper sulfate solution down the side of the inclined tube.

The result indicates the presence of \_\_\_\_\_

## B. SEPARATION OF CONSTITUENTS

1. **CASEIN AND FAT SEPARATION:** To a mixture of 50 ml. of whole milk and 50 ml. of water in a beaker, slowly add 10 per cent acetic acid, *drop by drop*, with constant stirring, until a flocky precipitate (casein and fat) separates and leaves a clear solution upon standing. Too much acid prevents the separation. What acid ordinarily sours and curdles milk?

What home nutrient is made from curd formed when milk sours?

Allow the curd to settle, filter, and save the whey (filtrate containing lactalbumin, mineral salts, and lactose) for 2.

(a) *Casein:* Remove the curd from the wet filter paper and press it as dry as possible between several thicknesses of dry toweling paper (or filter paper). Make the biuret test on a small portion.

Result shows the presence of \_\_\_\_\_  
Transfer the remaining curd to a test tube, cover with one-half a test tube of 95 per cent alcohol to remove adhering water. Shake it thoroughly and then discard the alcohol.

(b) *Fat:* Cover the curd again but this time with one-half a test tube of ether. *Turn out all gas flames near ether as the vapors ignite very readily.* With a glass rod stir the ether-casein-fat mixture for a minute or more. Pour the ether, or filter the ether extract into an evaporating dish. Allow the ether to evaporate spontaneously. Blowing upon the ether will hasten the evaporation. When no more ether will evaporate, make a spot with a drop of the residue on paper, hold up to the light and observe the *translucent*, greasy appearance of the fat. Dissolve the remaining fatty residue in 5 ml. of ether. Add 2 ml. of sodium alcoholate, carefully evaporate the ether, and then add 5 ml. of water. Pour into a test tube, add a piece of litmus paper, and then add  $H_2SO_4$ , drop by drop, until acid. Note the odor of volatile fatty acids. The odor is mostly due to \_\_\_\_\_ acid.

(c) *Rennin Precipitation of Casein:* As stated elsewhere, casein may also be precipitated by rennin. Fill a test tube about three-fourths full of whole milk and warm it to a little above body temperature by placing in a beaker of warm water (40 to 45° C.).

Dissolve a small amount, about one-tenth of a junket tablet, in 1 ml. of cold water, add it to the warm milk and allow to stand quietly for several minutes. Result? . . . . .

Commercial casein made in this way and treated with the proper bacteria is used to make what nutrient?

2. **LACTALBUMIN:** Place the whey (acetic acid filtrate saved from 1) in an evaporating dish and boil for at least a minute. Lactalbumin not precipitated by acetic acid will now be rendered insoluble. Filter and save the filtrate for the lactose and phosphate experiment. Of the two proteins in milk, lactalbumin differs from casein by being coagulated by \_\_\_\_\_ and not by dilute acids. Make the biuret test on the precipitated lactalbumin. Result?

3. **LACTOSE:** To one-half of the filtrate saved after the removal of albumin add 1 to 5 ml. of Benedict's solution and boil. The solution must be alkaline to litmus. A yellowish precipitate indicates the presence of lactose, and shows it has \_\_\_\_\_ properties.

4. **PHOSPHATE:** To the remaining half of the filtrate saved from the former test add about one-tenth of its volume of nitric acid. If a precipitate forms it is uncoagulated albumin and must be removed by filtration. Now add ammonium molybdate solution, warm, and allow to stand. The color of the precipitate is \_\_\_\_\_ and indicates the presence of a \_\_\_\_\_, which occurs as a salt of calcium in milk.

5. **CALCIUM (OPTIONAL):** Carefully evaporate 10 ml. of milk almost to dryness in an evaporating dish. Remove the wire gauze, add 2 ml.  $\text{HNO}_3$ , and heat directly with the flame until all the charred carbon has been oxidized to a white ash. To remove the last traces of unchanged carbon, hold the burner in your hand and direct the flame on the inside of the dish. Add  $\frac{1}{2}$  test tube of distilled water. Is the ash (inorganic) entirely soluble? Add about ten drops of  $\text{HCl}$ , heat to boiling, and filter into a test tube. Using a piece of litmus paper as an indicator make the filtrate

just basic with  $\text{NH}_4\text{OH}$ , and then just acid with acetic acid. To this solution add about 5 ml. of ammonium oxalate solution.

Calcium is slowly precipitated. Allow the test tube to stand undisturbed for 15 minutes, and then notice the amount of white precipitate. From your observation would you conclude that the amount of calcium in milk is high or low?

In what foods is calcium conspicuously absent?

A calcium deficiency in the diet results in poor development of

## **LABORATORY APPENDIX**

**I. Chemicals Required**

**II. Desirable Apparatus and Supplies**

**III. General Rules for Solubility**

**IV. Solubility Table**

**V. First Aid**

# 1. CHEMICALS REQUIRED FOR A MINIMUM OF FIFTY STUDENTS

(It is economical to buy in large quantities because the relative price of larger quantities is much less than when purchased in small quantities.)

<i>Quantity</i>	<i>Description</i>
1 lb	Acid, Acetic, 99.5 per cent, glacial C P
8 oz	Acid, Butyric, 98 per cent, C P
12 lb	Acid, Hydrochloric, sp gr 1.19, in 6 lb bottles, C P
1 liter	Acid, Hydrochloric, N/10
14 lb	Acid, Nitric, sp gr 1.42, in 7 lb bottles, C P
1 oz	Acid, Oleic, U S P
1 lb	Acid, Oxalic, C P
2 oz	Acid, Picric, C P
4 oz	Acid, Salicylic, Crystals, C P
18 lb	Acid, Sulfuric, sp gr 1.84, in 9 lb bottles C P
4 oz	Acid, Tannic, C P
8 oz	Acid, Tartaric, Crystals
8 oz	Albumin, dry egg
1 lb	Alcohol, Amyl, C P
1 gal	Alcohol, Ethyl 95 per cent, U S P
1 qt	Alcohol, Methyl, C P
8 vials	Alkaloid or Nitrazine test papers
4 oz	Aluminum Sulfate C P
4 oz	Ammonium Chloride, C P
8 lb	Ammonium Hydrate, C P sp gr 0.90, in 4-lb bottles
4 oz	Ammonium Molybdate
4 oz	Ammonium Oxalate, C P
1 lb	Ammonium Sulfate, C P
1 lb	Ammonium Tartrate, C P
1 lb	Amyl Acetate, pure
4 oz	Barium Chloride, C P
1 qt	Benedict's Solution qualitative
1 pt	Benedict's Solution quantitative
8 oz	Benzidine
1 lb	Calcium Carbonate Chips (marble)
4 oz	Calcium Chloride Anhydrous C P
4 oz	Calcium Hydroxide
3 lb	Calcium Hypochlorite technical (bleaching powder)
2 lb	Calcium Oxide (quicklime), lump
1 oz	Calcium Phosphate, pwd.
4 oz	Calcium Sulfate, calcined (plaster of Paris)
4 oz	Camphor, refined
4 lb	Carbon Disulfide, C P, in 1 lb bottles
3 lb	Carbon Tetrachloride, pure
4 oz	Casein (dry)
1 lb	Charcoal, Wood, animal
4 oz	Charcoal, Wood, stick, for blow pipe

<i>Quantity (Continued)</i>	<i>Description (Continued)</i>
2 lb	Chloroform, U S P
3 oz	Coffee
1 lb	Collodion (or cellophane sausage skins)
4 oz	Copper Metal, chips or punchings
4 oz	Copper Metal Wire, No 14, for making spiral
4 oz	Copper (ic) Chloride, crystals, C P
4 oz	Copper (ic) Oxide, powder, black, technical
1 oz	Copper (ic) Oxide, granular, C P
2 lb	Copper (ic) Sulfate crystals, U S P
4 oz	Dextrose, crystals C P
2 lb	Ether, Ethyl, U S P, in 1 lb cans
8 oz	Folin Wu Blood Sugar reagent
1 lb	Formaldehyde, 40 per cent solution, C P
1 qt	Gasoline
4 oz	Gelatin, granular
4 oz	Gelatin, Sheet
4 oz	Glycerol, U S P
5 lb	Hydrogen Peroxide, U S P, 3 per cent, in 1 lb bottles
4 oz	Iodine resublimed, C P
2 lb	Iron Powder
4 oz	Iron (ic) Chloride, C P, lumps
1 lb	Iron (ous) Sulfate, crystals, pure
2 oz	Iron (ous) Sulfide lump
4 oz	Junket tablets
1 lb	Karo Syrup
1 lb	Lactose (milk sugar), powder, C P
4 oz	Lead Acetate, normal, crystals, C P
4 oz	Litmus, cubes
8 oz	Magnesia Mixture
1 oz	Magnesium Metal, ribbon, $\frac{1}{8}$ in wide
1 lb	Magnesium Sulfate, crystals (Epsom salt)
1 lb	Manganese Dioxide, C P, powder
1 oz	Mercuric Oxide
10 gr	Mercurochrome, crystals or tablets
1 lb	Mercury (ic) Chloride, crystals C P
4 oz	Mercury (ic) Nitrate, C P
4 oz	Mercury (ous) Nitrate, C P
8 oz	Obermayer's solution
2 lb	Oil, Cottonseed
1 oz	Pancreatin, pure, powder
1 oz	Pepsin, U S P, powder
1 oz	Phenolphthalein, pure
1 oz	Phenylhydrazine hydrochloride
1 oz	Phosphorus, yellow, sticks
6 ft	Platinum Metal, wire, No 24
2 oz	Potassium Bisulfate, crystals, C P
1 lb	Potassium Bitartrate, powder, USP
4 oz	Potassium Bromide, C P



<i>Quantity (Continued)</i>	<i>Description (Continued)</i>
2 lb	Potassium Chlorate, crystals, C P
4 oz	Potassium Chloride, C P
1 lb	Potassium Dichromate C P
4 oz	Potassium Ferrocyanide, C P
4 oz	Potassium Hydrogen Sulfate
1 lb	Potassium Hydroxide, sticks purified
8 oz	Potassium Iodide, crystals, C P
1 oz	Potassium Metal, balls
2 lb	Potassium Nitrate, fine crystals
4 oz	Potassium Oxalate, powder
4 oz	Potassium Permanganate, C P
4 oz	Potassium Phosphate, C P
1 oz	Potassium Thiocyanate, C P
4 oz	Quinine
4 oz	Quinine Sulfate
25 Gm	Resorcin, Resublimed, C P
8 oz	Roberts' Reagent
1 lb	Saccharose, crystals, C P
4 oz	Silver Nitrate, crystals, U S P, C P
1 pt	Soap Solution
1 lb	Soda Lime, granular, pure
2 lb	Sodium Bicarbonate powder, C P
1 lb	Sodium Borate, powder, C P
2 lb	Sodium Carbonate, anhydrous, C P
5 lb	Sodium Chloride, pure (table salt)
5 lb	Sodium Hydroxide, sticks C P, in 1 lb bottles
2 lb	Sodium Hyposulfite ("hypo"), crystals, C P
2 oz	Sodium Metal
1 oz	Sodium Nitroprusside, C P
4 oz	Sodium Phosphate, dibasic, crystals, C P, secondary
1 lb	Sodium Phosphate, tribasic
4 oz	Sodium Potassium Tartrate Crystals, C P
4 oz	Sodium Sulfate, crystals, C P
1 oz	Sodium Tungstate
2 liters	Sorensen's buffer mixture
2 lb	Starch, Corn
1 lb	Steel Wool
1 lb	Sugar, Cane C P
8 oz	Sugar, Grape (dextrose)
2 oz	Sugar, Milk.
2 lb	Sulfur, Roll (brimstone), powder
4 oz	Tea
1 qt	Turpentine
1 lb	Zinc Metal, mossy, technical

## II. DESIRABLE APPARATUS AND SUPPLIES

In addition to the individual list of apparatus, page 638, for each student, the following general apparatus and supplies will be found desirable

Quantity	Description
1	Balance, inverted beam type, or triple scale—triple beam type
1	Bit, No 13, $\frac{3}{8}$ inch diameter
24	Bottles, dropping, Hood stopper, 2000 ml
Optional	Bottles, reagent, 8 oz, for acids and alkalies on laboratory tables
24	Candles (birthday)
1	Centrifuga (small table model)
24	Centrifuge tubes
1 yd	Cloth, muslin
1 lb	Coal, soft
100	Corks to fit bottles (6 oz)
300	Corks to fit test tubes
1 spool	Cotton Thread, No 10
2	Cylinder, graduated, 100 ml
1	Cylinder, graduated 500 ml
6	Fermentation Tube, on foot, small
12	File, triangular, 5 in
2	Forceps, steel, 4 in
15 ft	Glass rod, diam 5 mm
60 ft	Glass tubing, diam 6 mm
1	Graduate, cylindrical, 1000 ml
2	Graduate, cylindrical, 250 ml
1	Graduate, cylindrical, 500 ml
1	Knife, paring
1	Lancet, spring clamp, adjustable length
12	Magnet bar, length 15 cm
12	Magnifiers, reading glasses diam $2\frac{1}{2}$ in, with handles
72	Medicine droppers
1	Microscope
24	Mohr pipette, 2 ml
1 yd	Muslin, bleached
24	Needle holder, of brass nickel plated, adjustable screw chuck
1	Scissors
1 spool	Silk thread, white, heavy
24	<del>Slides and cover glasses</del>
2	Splint Wood, 100 in package.
6	Spoons, horn, length 4 in
6	Spoons, horn, length 6 in
2	Spoons, horn, length 8 in
1 ball	String (cotton)
24	Test tubes, 5 inch, with sidearm
4	Test tubes (25 x 150 mm)
24	Thermometers, 10° to 110° C
24	Urinometer.

Quantity (Continued)	Description (Continued)
4	Vogel Scale
24	Wing tops for burners
1 skein	Wool darning yarn white

### III. GENERAL RULES FOR SOLUBILITY

(a) All sodium, potassium, and ammonium compounds are soluble in water

(b) All nitrates, chlorates and acetates are soluble in water

(c) All chlorides are soluble, except those of silver, mercury (mercurous), and lead (lead slightly soluble)

(d) All sulfates are soluble, except those of lead, barium, strontium and calcium (calcium slightly soluble) The silver and the mercurous sulfates are only moderately soluble

(e) All carbonates are insoluble, except those of sodium, potassium, and ammonium

(f) All oxides and hydroxides are insoluble, except those of ammonium, sodium, potassium, and barium, calcium hydroxide is slightly soluble

## IV. SOLUBILITY TABLE

Since no salt is absolutely insoluble, the term "insoluble" is only relative (Scott's Standard Methods of Chemical Analysis, D Van Nostrand Co)

CATION	ANION																				
	F'	Cl'	Br'	I'	CN'	NO <sub>2</sub>	ClO <sub>3</sub> '	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> '	S'	CO <sub>3</sub> "	SiO <sub>3</sub> "	SO <sub>4</sub> "	CrO <sub>4</sub> "	$\left\{ \begin{matrix} \text{BO}_3' \\ \text{BO}_2' \end{matrix} \right\}$	PO <sub>4</sub> '	AsO <sub>4</sub> '	AsO <sub>3</sub> '	Fe(CN) <sub>6</sub> ""	Fe(CN) <sub>6</sub> "	OH'	
K	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	
Na'	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	
Li	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	
Ba	wa	W	W	W	wa	W	W	W	W	A	A	I	A	A	A	A	A	-	wa	-	
Sr	wa	W	W	W	W	W	W	W	W	A	A	I	wa	A	A	A	A	-	W	-	
Ca	wa	W	W	W	W	W	W	W	W	A	A	wa	wa	A	A	A	A	W	W	wa	
Mg	wa	W	W	W	W	W	W	wa	W	A	A	W	W	wa	A	A	A	W	W	-	
Al	W	W	W	W	-	W	W	W	-	-	wa	W	-	A	A	A	A	-	-	-	
Mn	A	W	W	W	A	W	W	wa	A	A	A	W	W	A	A	A	A	I	A	-	
Zn	wa	W	W	W	A	W	W	W	A	A	A	W	W	A	A	A	A	-	wa	-	
Cr	W	W	W	W	A	W	W	wa	-	-	A	W	A	A	A	A	A	-	-	-	
Cd	wa	W	W	W	A	W	W	W	A	A	A	W	W	wa	A	A	A	-	-	-	
Fe	wa	W	W	W	wa	W	W	W	A	A	A	W	-	A	A	A	A	I	I	-	
Fe	W	W	W	-	-	W	W	A	-	-	A	W	W	A	A	A	A	W	I	-	
Co	wa	W	W	W	wa	W	W	W	A	A	A	W	A	A	A	A	A	I	I	-	
Ni	wa	W	W	W	wa	W	W	W	A	A	A	W	A	A	A	A	A	I	I	-	
Sn	W	W	-	W	-	W	W	A	A	-	-	W	A	A	A	A	-	I	I	-	
Sn	W	W	-	W	-	-	-	-	A	-	-	-	-	-	A	A	A	-	I	-	
Pb	A	W	W	W	A	W	W	W	A	A	A	I	I	A	A	A	-	wa	A	-	
Cu'	A	W	W	I	I	W	W	W	A	A	-	W	W	A	A	A	A	-	I	-	
Sb	W	A	A	wa	-	-	-	A	A	-	-	A	A	-	A	A	A	-	-	-	
Bi	W	A	A	A	-	A	W	A	A	A	A	A	A	A	A	A	A	-	-	-	
Hg	-	I	I	I	-	W	W	A	-	A	-	wa	A	-	A	A	A	-	-	-	
Hg	wa	W	W	A	W	W	W	A	A	A	-	W	wa	-	A	A	A	-	-	-	
Ag	W	I	I	I	I	W	W	A	A	A	A	wa	A	A	A	A	A	A	I	-	
Pt	-	W	W	I	W	W	-	-	A	-	-	W	-	-	-	-	-	-	-	-	
Au	-	W	W	A	W	-	-	-	A	-	-	-	-	-	-	-	-	-	-	-	

ABBREVIATIONS W, soluble in water, A, soluble in acids wa slightly soluble in water, readily soluble in acids - difficulty soluble in water and in acids, I, insoluble in water and acids The metals are arranged in order of their electromotive series

## V. FIRST AID

A first aid cabinet\* should be in every laboratory. At least the following materials should be on hand for the *immediate* treatment of burns and cuts

- (a) Cotton— $\frac{1}{2}$  pound roll
- (b) Plain sterile gauze—to apply to wounds and burns
- (c) Sterile gauze bandages—2 inches by 10 yards
- (d) Adhesive tape— $\frac{1}{2}$  inch by 10 yards
- (e) Sodium bicarbonate (baking soda), tannic acid jelly, or picric acid burn emollient. (These substances are used for burns)
- (f) Saturated boric acid solution—this is about one teaspoonful of boric acid to a glass of water
- (g) Tincture of iodine, 3 per cent
- (h) Aspirin tablets, five grains each (Two tablets may be given for pain pending the arrival of the doctor)
- (i) Aromatic spirits of ammonia
- (j) Tourniquet to stop hemorrhage (A length of rubber tubing makes an excellent tourniquet. A tourniquet should be loosened every few minutes or there is danger of causing gangrene)

### BURNS

Burns are classified into three degrees. In a first degree burn, associated with redness, the skin is never broken. In a second degree burn a blister occurs while in a third degree burn there is a destruction and involvement of the tissues below the burn. Never use oil or any greasy substance on badly blistered or broken skin, because of the danger of infection, and interfering with the treatments listed below or those of a physician.

On a burned area are formed toxic substances, which upon absorption injure the kidneys. In severe cases of burns death results, due to uremia. Tannic acid or picric acid prevents the absorption by precipitating the injured tissues and forming a firm coagulum over the surface, and thus prevents the absorption of these toxic proteins, and at the same time acts as an antiseptic, as well as relieving pain by excluding air. Days later when the coagulum separates it leaves a healed epidermis in superficial burns, and a clean granulating surface in deeper burns.

*From Heat.* Dress with either of (e) and bandage.

*From Acids.* Wash thoroughly with water, treat with dilute sodium bicarbonate (5 per cent solution) and bandage.

*From Alkalies.* Wash thoroughly with water, treat with (f) and bandage.

*In the Eye.* Wash thoroughly with water, treat with dilute sodium bicarbonate (5 per cent solution) if an acid burn or (f) if an alkali burn.

### CUTS

*From Glass.* Wash with water, treat with (g) and bandage.

\* First Aid Cabinet prepared by the Fisher Scientific Co., Pittsburgh, Pa., which company has for distribution an excellent Laboratory Emergency Chart.

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